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Batch-Type Adsorption Procedures for Estimating Soil Attenuation of Chemicals Draft Technical Resource Document for Public Comment

Illinois State Geological Survey Div., Champaign

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BATCH-TYPE ADSORPTION PROCEDURES FOR ESTIMATING SOIL ATTENUATION OF CHEMICALS

Draft Technical Resource Document
for Public Comment

OFFICE OF SOLID WASTE AND EMERGENCY RESPONSE
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

Hazardous Waste Engineering Research Laboratory
Office of Research and Development
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This Technical Resource Document (TRD) describes a number of laboratory batch procedures for assessing the capacity of soils and soil components of liners for waste management facilities to attenuate chemical constituents from solution. Procedures for both organic and inortanic constituents are described, and their scientific basis and rationale are documented. Examples are included to demonstrate the application of the procedures and the use of the data in designing soil liners for pollutant retention.

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DISCLAIMER

This report was prepared by W. R. Roy, I. G. Krapac, S. F. J. Chou, and R. A. Griffin of the Illinois State Geological Survey, Champaign, Illinois, under Cooperative Agreement CR810245. The EPA Project Officer was M. H. Roulier of the Hazardous Waste Engineering Research Laboratory, Cincinnati, Ohio.

This is a draft report that is being released by EPA for public comment on the accuracy and usefulness of the information in it. The report has received extensive technical review, but the Agency's peer and administrative review process has not yet been completed. Therefore, it does not necessarily reflect the views or policies of the Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWARD

The Environmental Protection Agency was created because of increasing public and governmental concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of the environment and the interplay of its components require a concentrated and integrated attack on the problem.

The Office of Solid Waste is responsible for issuing regulations and guidelines on the proper treatment, storage, and disposal of hazardous wastes, in order to protect human health and the environment from the potential harm associated with improper management of these wastes. These regulations are supplemented by guidance manuals, technical guidelines, and technical resource documents, made available to assist the regulated community and facility designers in understanding the scope of the regulatory program. Publications like this one provide facility designers with state-of-the-art information on design and performance evaluation techniques.

This Technical Resource Document (TRD) describes a number of laboratory batch procedures for assessing the capacity of soils and soil components of liners for waste management facilities to attenuate chemical constituents from solution. Procedures for both organic and inorganic constituents are described, and their scientific basis and rationale are documented. Examples are included to demonstrate the application of the procedures and the use of the data in designing soil liners for pollutant retention.

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Director, Office of Solid Waste
U.S. Environmental Protection Agency

PREFACE

Subtitle C of the Resource Conservation and Recovery Act (RCRA) requires the U.S. Environmental Protection Agency (EPA) to establish a Federal hazardous waste management program. This program must ensure that hazardous wastes are handled safely from generation until final disposition. EPA issued a series of hazardous waste regulations under Subtitle C of RCRA that are published in 40 Code of Federal Regulations (CFR) 260 through 265 and 122 through 124.

Parts 264 and 265 of 40 CFR contain standards applicable to owners and operators of all facilities that treat, store, or dispose of hazardous wastes. Wastes are idnetified or listed as hazardous under 40 CFR Part 261. Part 264 standards are implemented through permits issued by authorized States or EPA according to 40 CFR Part 122 and Part 124 regulations. Land treatment, storage, and diposal (LTSD) regulations in 40 CFR Part 264 issued on July 26, 1982, establish performance standards for hazardous waste landfills, surface impoundments, land treatment units, and waste piles.

EPA is developing three types of documents for preparers and reviewers of permit applications for hazardous waste LTSD facilities. These types include RCRA Technical Guidance Documents, Permit Guidance Manuals, and Technical Resource Documents (TRD's).

The RCRA Tehnical Guidance Documents present design and operating specifications or design evaluation techniques that generally comply with or demonstrate compliance with the Design and Operating Requirements and the Closure and Post-Closure Requirements of Part 264.

The Permit Guidance Manuals are being developed to describe the permit application information the Agency seeks and to provide guidance to applicants and permit writers in addressing information requirements. These manuals will include a discussion of each step in the permitting process and a description of each set of specifications that must be considered for inclusion in the permit.

The Technical Resource Documents present state-of-the-art summaries of technologies and evaluation techniques determined by the Agency to consitiute good engineering designs, practices, and procedures. They support the RCRA Technical Guidance Documents and Permit Guidance Manuals in certain areas (i.e., liners, leachate management, closure covers, and water balance) by describing current technologies and methods for designing hazardous waste facilities or for evaluating the performance of a facility design. although emphasis is given to hazardous waste facilities, the information presented in these TRD's may be used for designing and operating nonhazardous waste LTSD facilities as well. Whereas the RCRA Technical Guidance Documents and Permit Guidance Manuals are directly related to the regulations, the information in these TRD's covers a broader perspective and should not be used to interpret the requirements of the regulations.

This document is a first edition draft being made available for public review and comment. It has undergone review by recognized experts in the technical areas covered, but Agency peer review processing has not yet been completed. Public comment is desired on the accuracy and usefulness of the information presented in this document. Comments received will be evaluated, and suggestions for improvement will be incorporated, wherever feasible, before publication of the second edition.

One original and one copy of all comments on this document should be addressed to: Docket Clerk (Room S-212A), Office of Solid Waste (WH-562), U.S. Environmental Protection Agency, 401 "M" Street, S.W., Washington, D.C. 20460. Comments should identify the document by title and number; e.g. "Batch-Type Adsorption Procedures for Estimating Soil Attenuation of Chemicals" (EPA/530-SW-87-006).

ABSTRACT

This document contains laboratory procedures and guidelines for conducting adsorption experiments using batch equilibrium techniques to study soil attenuation of chemicals dissolved in solution (solutes). The procedures were designed for routine use, and may be used to generate data for the construction of equilibrium adsorption isotherms or curves. Procedures for inorganic and organic solutes, and volatile organic solutes are given.

The scientific basis and rationale for each procedural step is discussed in detail, and was based on both the scientific literature and by procedural development and testing by the authors and other cooperating laboratories, using several different types of soil materials and solutes. The application of major procedural steps and concepts is illustrated by examples, including the application of batch adsorption data in calculations of solute movement through compacted landfill liners, particularly for estimating the thickness of liner required for pollutant retention.

CONTENTS

page
Disclaimer.. ii
Foreward.. iii
Preface... iv
Abstract.. vi
Figures... viii
Tables.. xii
Acknowledgments... xiv

INTRODUCTION.. 1

SECTION

1. Adsorption forces and mechanisms..................... 5
2. Effects of adsorbent preparation..................... 8
3. Effects of temperature............................... 17
4. Stability of nonionic solutes in solution............ 23
5. Effects of solution pH............................... 28
6. Effects of ionic strength............................ 36
7. Effects of phase separation.......................... 42
8. Effects of the method of mixing...................... 46
9: Selection of a soil:solution ratio for ionic solutes. 52
10. Selection of a soil:solution ratio for nonionic solutes.. 60
11. Effects of the soil:solution ratio.................. 68
12. Constant and variable soil:solution ratios.......... 89
13. Determination of the equilibrium time............... 97
14. Construction of adsorption isotherms (curves)....... 108
15. Selection of adsorption equations................... 116
16. Application of adsorption data...................... 119
17. Laboratory procedures for collecting adsorption data.. 133

References.. 162

APPENDIX A. Summary and chemical composition of the adsorbent soils and clays used in this study........................ 173

B. Chemical composition of the metallic waste extract used in this study and associated adsorption isotherms.... 179

LIST OF FIGURES

page

Figure 1. Effect of air-drying on the concentration of exchangeable manganese.......... 10

Figure 2. Relationship between the concentration of exchangeable potassium in the Harpster clay loam and moisture content.......... 10

Figure 3. Effect of oven-drying at 105°C on the concentration of water soluble organic carbon in an Israeli calcareous clay loam.......... 12

Figure 4. Adsorption isotherm of acetophenone by fresh field moist and air-dried samples of Crane Island alluvium..... 15

Figure 5. Arsenate adsorption isotherms by Catlin at 15°C, 25°C and 35°C.......... 19

Figure 6. Zinc, copper, and cadmium adsorption from a DuPage County landfill leachate by kaolinite at 25°C at various pH levels.......... 29

Figure 7. Chromium (VI) adsorption by kaolinite at 25°C at various pH levels.......... 31

Figure 8. Langmuir-type maximum (mM/g) for the adsorption of arsenic as As(V) and As(III) by amorphous iron hydroxide.......... 32

Figure 9. Effect of pH on the adsorption of triazines by a Ca-montmorillonite sample.......... 33

Figure 10. Effect of pH on the adsorption of different ionizable organic solutes by an illite sample.......... 33

Figure 11. The adsorption behavior of the PCB Aroclor 1242 by a synthetic goethite, a Cecil clay, and EPA-14 soil samples as a function of pH at 24°C.......... 35

Figure 12. Ratio of concentration to activity versus ionic strength for some common ions.......... 37

Figure 13. Effect of pore size and number of continuative filtrations of 100-mL aliquots of HCB-saturated water on the concentration of HCB in filtrates.......... 43

Figure 14. Distribution of arsenic concentrations in solutions that were either centrifuged or filtered.......... 44

Figure 15. The National Bureau of Standards Rotary Extractor........ 48

page

Figure 16. Distribution of arsenate concentrations after 24 hours of contact with different soil materials as a function of soil:solution ratio.................... 55

Figure 17. Distribution of cadmium concentrations after 24 hours of contact with different soil materials as a function of soil:solution ratio.................... 56

Figure 18. Adsorption isotherm of o-xylene by Catlin at 23°C........ 63

Figure 19. Adsorption isotherms of dichloroethane and tetrachloroethylene by Catlin at 23°C.................... 64

Figure 20. Relationship between the linear Freundlich constant (K_d) and soil:solution ratio, as a function of percent adsorption (lower range)........... 66

Figure 21. Relationship between the linear Freundlich constant (K_d) and soil:solution ratio, as a function of percent adsorption (upper range)........... 67

Figure 22. Effect of soil:solution ratio on cadmium adsorption by a Sangamon paleosol sample................. 71

Figure 23. Cadmium adsorption by a Sangamon paleosol sample......... 73

Figure 24. Distribution of pH values of arsenate solutions after 24 hours of contact with different soil materials as a function of soil:solution ratio........... 75

Figure 25. Distribution of pH values of cadmium solutions after 24 hours of contact with different soil materials, as a function of soil:solution ratio.......... 76

Figure 26. Distribution of pH values of solutions of the zinc slurry extract after 24 hours of contact with two soil samples as a function of soil:solution ratio........ 78

Figure 27. Distribution of the ionic strength of solution containing either arsenate or cadmium after 24 hours of contact as a function of soil:solution ratio.......... 79

Figure 28. Freundlich constant (K_f) for two PCB isomers vs. sediment concentration with and without prewashing to remove nonsettling particles.......................... 81

Figure 29. The Freundlich constant (K_f) for the adsorption of Aroclor 1242 by four different soils as a function of soil:solution ratio.......................... 83

Figure 30. Aroclor 1242 adsorption isotherms by five soils at various soil:solution ratios.......................... 84

page

Figure 31. Adsorption of dieldrin, tetrachloroethylene, and 1,2-dichloroethane by Catlin at various soil:solution ratios.................................... 85

Figure 32. Adsorption of Aroclor 1242 by altered Vandalia till and unaltered Vandalia till at various soil:solution ratios.................................... 87

Figure 33. Distribution of exponents (1/n) and Freundlich constants (K_f) associated with arsenic, cadmium, lead, and PCB (Aroclor 1242) adsorption isotherms........ 91

Figure 34. Cadmium adsorption isotherm with a Vandalia till sample (unaltered) with the amount adsorbed associated with each isotherm data shown................. 93

Figure 35. Distribution of cadmium adsorption data by a Tifton sandy loam... 94

Figure 36. Distribution of arsenate adsorption data by different soil samples using different soil:solution ratios.................................... 96

Figure 37. The adsorption behavior of cadmium by five soil materials as a function of contact time.................. 99

Figure 38. The adsorption behavior of arsenic by 11 different soil materials as a function of contact time............. 100

Figure 39. Determination of equilibration time of Ba, Pb, and Zn from a laboratory extract of the Sandoval Zinc slurry with the Sangamon Paleosol and the Cecil clay sample.................................. 104

Figure 40. The adsorption behavior of o-xylene, dichloroethane, and tetrachloroethylene by Catlin as a function of contact time.. 106

Figure 41. The adsorption of arsenic by a kaolinite clay sample as described by the traditional linear Langmuir, double-reciprocal Langmuir, and the Freundlich Equation............................. 118

Figure 42. Lead adsorption by Cecil clay loam described by a linear Freundlich equation through the origin.......... 125

Figure 43. Predicted distance of lead migration in Cecil clay loam based on three approaches........................... 129

Figure 44. Flow diagram for the procedures for the generation of batch adsorption data...................... 134

Figure B-1. Barium adsorption isotherm with the Sangamon Paleosol from the metallic waste extract................ 181

Figure B-2. Lead adsorption isotherms of two soils using the metallic waste extract............................... 182

Figure B-3. Zinc adsorption isotherms of two soils using the metallic waste extract............................... 183

LIST OF TABLES

page

Table 1. Effect of drying on exchangeable Mn in four Hawaiian soils.......... 9

Table 2. pH of soil-water slurries (1:2 v/v) made with field-moist samples compared to those that were oven-dried at 110°C.......... 13

Table 3. Effect of sample pretreatment on the Freundlich partition coefficients (K_f).......... 14

Table 4. Effect of temperature on Freundlich adsorption constants (K_f) for phenanthrene and α-naphthol.......... 20

Table 5. Results of first ASTM sensitivity analysis 47

Table 6. Cadmium adsorption data from the 2nd ASTM interlaboratory sensitivity analysis using a NBS rotary extractor as the mixing method.......... 49

Table 7. Arsenic adsorption data from the 2nd ASTM interlaboratory sensitivity analysis using a NBS rotary extractor as the mixing method.......... 50

Table 8. Soil:solution ratio determination for the Sangamon soil and Vandalia ablation till using cadmium as the adsorbate.......... 53

Table 9. Determination of soil:solution ratios for the Sangamon Paleosol and the Cecil clay loam sample using an extract of the Sandoval zinc slurry.......... 58

Table 10. Determination of equilibration times for the adsorption of arsenate by soil materials.......... 102

Table 11. Determination of equilibration times for the adsorption of Ba, Pb, and Zn from a Sandoval zinc slurry extract by the Sangamon paleosol and Cecil clay 103

Table 12. Determination of equilibration time for the adsorption of the PCB Aroclor 1242 by Catlin.......... 107

Table 13. Data reduction for arsenic adsorption by a kaolinite clay sample.......... 110

Table 14. Lead adsorption data using a $Pb(NO_3)_2$ salt and the Cecil clay.......... 123

Table 15. Summary of approaches to estimate minimum liner thicknesses.......... 132

Table A-1. Summary of adsorbents.................................... 175

Table A-2. Summary of selected physicochemical characteristics of clays and soils used in the development of TRD........ 176

Table A-3. Summary of major element composition (in oxide form) of clay and soils used in the development of TRD.. 177

Table A-4. Summary of trace element concentrations in the clays and soils used in the development of the TRD....... 178

Table B-1. Chemical constituent concentrations obtained by the ASTM-A (water shake extraction) performed on the Sandoval zinc slurry.............................. 180

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INTRODUCTION

The capacity of geological materials to attenuate potential pollutants has been studied by many researchers, especially during the last 30 years. One of the potential applications of information from such studies is the design and evaluation of compacted soil or clay liners for attenuation of chemical constituents of leachates from waste management facilities such as landfills and surface impoundments. This Technical Resource Document (TRD) describes a number of laboratory batch procedures for assessing the capacity of soils to adsorb (attenuate) chemicals from solution. Procedures for both organic and inorganic constituents are described and their scientific basis and rationale are documented. Examples are included to demonstrate the application of the procedures, and the use of the adsorption data in designing soil liners for pollutant attenuation.

The batch adsorption or batch equilibration technique has often been used in laboratory studies to assess the capacity of soils and soil components to attenuate chemical constituents in solution. However, the batch procedures that have been used vary considerably in terms of experimental conditions and research objectives and, in some cases, may yield different results even when the same soils, solutes and concentrations are studied.

In principle, the batch adsorption technique is relatively simple, accounting, in part, for its popularity. This technique consists of mixing an aqueous solution containing solutes of known composition and concentrations with a given mass of adsorbent for a period of time. The solution is then separated from the adsorbent and chemically analyzed to determine changes in solute concentration. The amount of solute adsorbed by the adsorbent is assumed to be the difference between the initial concentration (before contact with the adsorbent) and the solute concentration after the mixing period.

While the approach is relatively simple, there are a number of experimental parameters that may affect the adsorption of a given constituent. For inorganic solutes, these parameters include contact time, temperature, method of mixing, soil:solution ratio, adsorbent moisture content, solution pH, hydrolysis, and the composition and concentration of other dissolved constituents in the solution (White, 1966; Barrow and Shaw, 1975, 1979; Helyar et al., 1976; Hope and Syers, 1976; Griffin and Au, 1977; Barrow, 1978; Ainsworth et al., 1984; and Roy et al., 1984, 1985). For organic solutes, similar parameters may also affect adsorption (Bailey and White, 1970; Grover and Hance, 1970; Dao and Lavy, 1978; Koskinen and Cheng, 1983; and Horzempa and DiToro, 1983). In addition, dissolved organic carbon, adsorbate volatility, photodegradation, biodegradation, and compound stability can also affect adsorption data associated with organic solutes (Harris and Warren, 1964; Scott et al., 1981; and Chou and Griffin, 1983).

Equilibration time, a basic experimental parameter in the batch techniques cited above, has varied from 30 minutes to 2 weeks. Soil:solution ratios used in batch procedures have varied from very dilute systems (1:100,000) to 1:1 pastes. These particular experimental conditions were probably appropriate for the specific system under study, and appropriate for the intended use of the data. However, these diverse differences in experimental conditions may make comparisons of data between studies difficult. Moreover, there are currently no standardized batch adsorption procedures designed for routine use with the exception of the procedural guidelines outlined in EPA (1982) and the standard methods currently under development of the American Society for Testing and Materials (ASTM) D-18, D-34, and E-47. Results from recent D-34.02 round-robin testing of batch sorption procedures indicated coefficients of variation of greater than 140% during initial testing, which were reduced to less than 10% by application of standard procedures and equipment between laboratories (Griffin et al., 1985). The experience gained during those interlaboratory testing programs and the interactions with the scientists and laboratories affiliated with ASTM have been incorporated into this document. The proposed ASTM 24-hour batch adsorption procedure has been reviewed and voted upon by the committee members. Comments have been received from 96 individuals who are active in research, government, industry, and waste management.

Furthermore, there are very few well documented and comprehensive sources that can be consulted for conducting batch adsorption experiments. The purpose of this Technical Resource Document (TRD) is to describe a number of batch adsorption procedures for both inorganic and organic solutes, to document their scientific basis and rationale, and to recommend procedural steps that are best supported by current information. This TRD also contains numerous examples to demonstrate the application of each procedural step. Section 16 demonstrates how adsorption data can be used in designing or evaluating soil liners for pollutant retention and discusses some cases where this has been done. The last section of this report contains the actual procedures written without narrative discussion. The reader should study the preceding sections before attempting these procedures.

Most of the procedural steps recommended here have been tested in the author's laboratory using a variety of soils, solutions containing several solutes, and aqueous extracts of actual wastes. Characteristics of the soils, clays, and waste are described in appendices to this document.

The information in Section 1 on adsorption forces and mechanisms was taken from an open file report entitled "Interaction of Organic Solvents with Saturated Soil Water Systems" that was written by Dr. R. A. Griffin and

Dr. W. R. Roy (April 1985) for the Environmental Institute for Waste Management Studies, University of Alabama. Information and references for other sections have also been drawn from that report.

The collection of accurate and meaningful adsorption data is not a simple task. Even though the procedures described here were intended to be fairly easy to use and precise, it is inevitable that some "scatter" in data will occur, and the origins of the deviations will elude any clear-cut explanations. The investigator is encouraged to persevere and repeat the procedures as the situation demands. The perseverance is well warranted as the acquisition of high quality adsorption data is essential in predicting, and thus protecting, the quality of ground and surface waters that must co-exist with the by-products of our civilization.

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SECTION 1: ADSORPTION FORCES AND MECHANISMS

Before undertaking adsorption studies, it may be informative to briefly review the physical chemical forces and mechanisms that are thought to be responsible for the adsorption of ions and molecules.

Adsorption from solution at the solid-liquid interface is a complex and imperfectly understood phenomenon. These physical chemical forces may be broken down into eight categories (after Reinbold et al., 1979; Griffin and Roy, 1985; and a paper containing other useful references by Voice and Weber, 1983):

1. London-van der Waals. There are attractive forces that arise from momentary dipoles about atoms or molecules caused by small perturbations of electronic motions. These dipoles induce small dipoles in neighboring atoms of opposite sign. Although the momentary dipoles and induced dipoles are constantly changing position and sign, the net result is a weak attraction (4 to 8 KJoule/mole for small molecules and atoms). These forces are important in adsorption of organics and are generally attributed to explaining the non-ideal behavior in gases. They also have been partially treated by quantum mechanical perturbation theory, using polarizabilities, ionization potentials, and the magnetic susceptibilities of the interacting atoms to explain various phenomena such as adsorption.

2. Coulombic-electrostatic-chemical. An electrostatic force resulting from a charged surface due to isomorphous substitution in the mineral lattice (permanent charge) or protonation of surface oxygen and OH groups (pH-dependent charge) and an oppositely charged species to maintain the electroneutrality of the surface is important in cation exchange reactions in soils. In layer silicates, substitution of octahedrally or tetrahedrally coordinated cations by cations of lower valence results in a net negative charge. This excess charge can bring about the formation of a diffuse layer of positively charged atoms

or molecules about the colloid whose density is greater at the surface, then exponentially decreases to the level of the bulk solution. This type of reaction is important in adsorption of both inorganic ions and ionized organic molecules.

3. Hydrogen bonding. This type of interaction is where a hydrogen atom is bonded to two or more other atoms in that the "bond" is generally conceived as an induced dipole phenomena. There is no universal agreement on the best description of the hydrogen bond (Huheey, 1978), but it may be considered as the asymmetric electronic distribution of the 1s electron of the hydrogen atom by very electronegative atoms (such as F, O, S, Cl, etc.). There are reasons to believe that more is involved in hydrogen bonding than simply an exaggerated dipole-dipole or an ion-dipole interaction due to the inability of these concepts to account for molecular geometry in some cases (see Huheey, 1978; Cotton and Wilkinson, 1980). H-bonds may be in reality delocalized covalent bonds, i.e., resonance bonds or multiple-center bonds (Huheey, 1978). The energy of this attraction ranges from 8 to 42 KJoule/mole.

4. Ligand exchange-anion penetration-coordination. Many atoms or molecules form coordinated complexes with ligands that range in complexity from simple linear molecules to extensive chelate complexes. The coordinated complexes may carry a net charge which may be localized on some part of the complex. These complexes may be in turn bonded to surfaces by H-bonding or by polyvalent cation bridges linking the complex to a charged surface. The possible geometrical arrangements of coordinated complexes bonded to mineral faces is diverse. The bonded coordinated complexes may be displaced by other coordinated complexes that better satisfy electroneutrality requirements (i.e., are stronger complexing agents) while being constrained by steric limitations. The energy of ligand exchange reactions with inorganic ions ranges from 8 to 60 KJoule/mole.

5. Chemisorption. In this adsorption process an actual chemical bond, usually covalent, is formed between the molecule and the surface atoms. A molecule undergoing chemisorption may lose its identity as the atoms are rearranged, forming new compounds at the demand of the unsatisifed valences of the surface atoms. The enthalpy of chemisorption ($-\Delta H > 29$ KJoule/mole) is much greater than physical adsorption. The basis of much catalytic activity at surfaces is that chemisorption may organize molecules into forms that readily undergo reactions. It is often difficult to distinguish between chemisorption and physical adsorption because a chemisorbed layer may have a physically adsorbed layer upon it. Moreover, some ligand exchange reactions are chemisorption processes.

6. Dipole-dipole or orientation energy. This results from the attraction of a permanent dipole for another permanent dipole. The resulting energy of attraction is less than 8 KJoule/mole.

7. Induction or dipole-induced dipole. This results from the attraction of an induced dipole brought about by either a permanent dipole or a charged site or species. The energy of attraction is less than 8 KJoule/mole, but this force often adds to coulombic interactions.

8. The hydrophobic effect. The exact nature of this adsorption mechanism is uncertain. It is the view of some investigators that hydrophobic adsorption is primarily an entropically-driven mechanism brought about by the destruction of the physical cavity occupied by the solute in the solvent, and from the partial loss of structured water molecules about the solute, ordered by van der Waals forces (Horvath et al., 1976; Sinanoglu and Abdulnur, 1965). Other researchers feel that the hydrophobic effect is the result of simple partitioning. Nonpolar organic solutes tend to migrate from the aqueous phase to hydrophobic surfaces on the adsorbent (Dzombak and Luthy, 1984, Chiou et al., 1979, 1983; see also Griffin and Roy, 1985).

SECTION 2: EFFECTS OF ADSORBENT PREPARATION

The process of preparing samples taken in the field for laboratory investigations can have a direct influence on analytical results. Adsorbent samples (i.e., soils, clays, etc.) are usually dried so that they can be homogenized and stored until needed. However, studies have shown that the method of drying the sample may alter its chemical properties which in turn can influence the results of batch adsorption procedures.

An early paper by Fujimoto and Sherman (1945) concluded that the concentration of exchangeable manganese in twenty-three Hawaiian soils tended to increase as the samples were dried. A portion of their results is given in Table 1. The changes that occurred between field moist and air drying were, however, minimal compared to the changes that occurred upon oven drying or autoclaving. They also found that the amount of exchangeable manganese tended to increase as the duration of air-drying increased until about 8 to 10 weeks (Fig. 1).

Luebs et al. (1956) found that the amount of exchangeable K^+ in 13 Iowa soils increased when the soils were air-dried for 2 months. However, a reduction in the moisture content of the soils from 25% to 10% was required before appreciable changes in exchangeable K^+ could be detected (Fig. 2).

Drying soil samples may also have an effect on the stability of the organic matter in soils. Air-drying soils generally stimulates soil microorganism respiration when they are re-wetted, and Stevenson (1956) concluded that the degree of metabolic activity varies directly with the concentrations of free amino acids and other nitrogenous materials released during air-drying.

Birch (1958), continuing the work of earlier investigators, found that when either oven-dried or air-dried soils were re-moistened, a portion of the

Table 1. Effect of drying on exchangeable Mn in four Hawaiian soils (from Fujimoto and Sherman, 1945).

Location of Soil	pH(1:1)[1]	Field Moisture	Air-dried	Oven-dried[2]	Autoclaved[3]
		-------------Mn concentration (mg/L)--------------			
Kemoo	4.2	3.4	4.5	621.2	374.8
Koko Head	7.1	0.0	4.3	29.4	ND[4]
Kahuku	7.6	0.0	0.4	11.7	367.9
Waimanalo	8.6	0.5	0.4	1.2	ND

[1] pH of a 1:1 soil:water suspension

[2] Oven-dried for 24 hours at 105°C

[3] Autoclaved for 3 hours at 15 pounds pressure

[4] Not determined

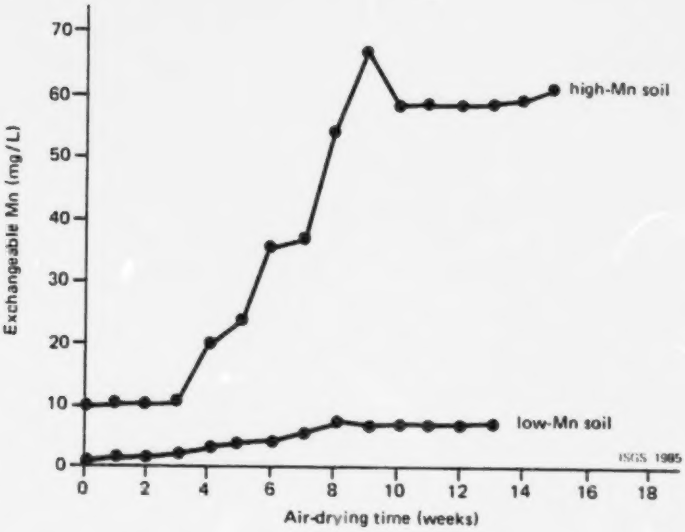

Figure 1. Effect of air-drying on the concentration of exchangeable manganese (adapted from Fujimoto and Sherman, 1945).

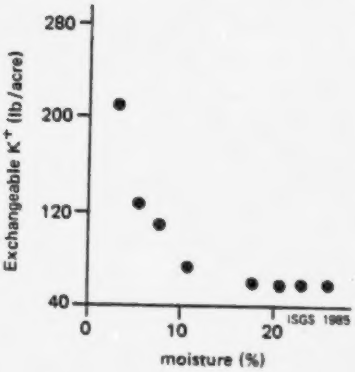

Figure 2. Relationship between the concentration of exchangeable potassium in the Harpster clay loam and moisture content (adapted from Luebs et al., 1956).

organic matter dissolved and the magnitude of this decomposition depended directly on the amount of organic matter present in the soil. Birch (1959) later concluded that this decomposition following re-wetting was primarily due to microbial decomposition of water soluble organic matter.

An alternative hypothesis was proposed by Raveh and Avinimelech (1978). They envisioned that when organic macromolecules are in natural pedological settings, they are aggregated by hydrogen bonds. When soils are dried, the evaporation of water disrupts the H-bonds and the stability of the organic matter decreases. They also observed that the amount of water soluble carbon in aqueous extracts increased as the length of oven drying periods at 105°C increased (Fig. 3).

According to Bartlett and James (1980), one of the most noticeable effects of air-drying soils is an increase in the yellow or amber color of extracts, attributable to the amount of organic matter made soluble by drying. They also found that the amounts of Al, Fe, and Mn in NH_4OAc extracts (pH 4.8) of a soil subjected to 40°C for 12 hours were greater than those extracted from moist samples at field moisture of the same soil.

Drying soil samples has been reported to change the pH of the soil (or soil reaction). Van Lierop and MacKenzie (1977) found that oven-drying soil samples at 110°C tended to result in lower pHs relative to the pHs of field-moist samples of the same soils. The change in pH varied from 0.3 to 1.1 pH units (Table 2). Raven and Avinimelech (1978) suggested that this increase in acidity was due to the exposure of fresh organic surfaces that contained acidic groups that were sterically hindered before drying. The increase in surface acidity was also considered by Mortland and Raman (1968) who hypothesized a different mechanism; as the samples are dried, adsorbed cations more strongly polarize the residual water molecules, making them more acidic than free water.

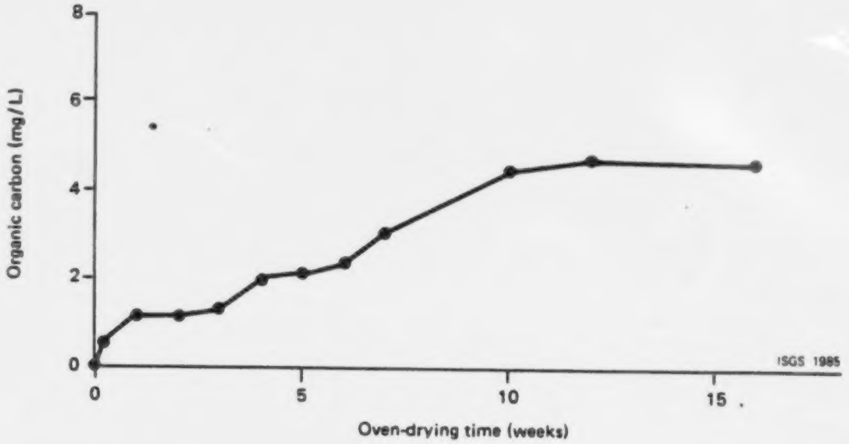

Figure 3. Effect of oven-drying at 105°C on the concentration of water soluble organic carbon in an Israeli calcareous clay loam (adapted from Raveh and Avnimelech, 1978).

Table 2. pH of soil-water slurries (1:2 v/v) made with field-moist (FM) samples compared to those that were oven-dried at 110°C (OD) (from van Lierop and MacKenzie, 1977).

Soil	FM	OD	ΔpH
Demers	4.0	3.0	1.0
J.I.v.	4.2	3.7	0.5
J.I.-1	5.5	5.2	0.3
J.I.-2	6.2	5.8	0.4
HDE	4.5	4.0	0.5
SB	4.1	3.7	0.4
Bigras v.	4.2	4.1	0.1
Leh. v.	4.2	3.9	0.3
Lamb.	6.7	5.6	1.1
Mac.	6.3	5.8	0.5

Other studies have demonstrated that drying samples lowers the ability of a soil to oxidize chromium (Bartlett and James, 1980), and can influence denitrification studies (Patten et al., 1980; Soulides and Allison, 1961) and other soil chemical processes that may have an indirect effect on batch adsorption studies.

Direct effects of adsorbent preparation have also been documented; Ashton and Sheets (1959) found that the herbicide ethyl N,N-di-n-propylthiolcarbamate (EPTC) was adsorbed as a vapor to a greater extent by air-dried soils than soils that were moist. The adsorption of EPTC may have been suppressed at higher moisture contents due to the competition of the EPTC vapor and water molecules for adsorption sites. Dao and Lavy (1978) observed that the adsorption of atrazine by Nebraskan soils decreased with an increase in soil moisture. They also suggested that competition between the atrazine and water could account for this relationship.

Oven-drying may increase the hydrophobicity of soils which, in turn, would enhance the adsorbent's affinity for hydrophobic solutes. It has been established that forest fires can increase the hydrophobicity of soil materials near the surface. Heat-induced hydrophobicity studies by Debano et al. (1976) suggested that temperatures as low as 98° to 118°C for an exposure time of as little as 5 minutes can increase the hydrophobicity of a sample as measured by water drop penetration time. It is not certain whether this heat-induced hydrophobicity will influence adsorption results obtained by batch techniques. Hassett et al. (1980), for example, found that the adsorption behavior of acetophenone on two alluvial silt samples was not significantly affected by various drying techniques (Table 3). Oven-drying a Sangamon River sample appeared to generate a slightly lower Freundlich constant (K_f) relative to the values for field moist, frozen, air-dried or freeze-dried samples, but the difference was not significant at the 5% level of probability. As shown in Figure 4, the distribution of isotherm points generated from air-dried samples tended to be similar to those from fresh field moist samples.

In contrast, Bartlett and James (1980) found that a soil sample which had been oven-dried at 40°C adsorbed more phosphate during a six-hour equilibration than samples which were kept moist. Harada and Wada (1974) reported that air-drying their soil samples resulted in slight but significant increases in

Table 3. Effect of sample pretreatment on the Freundlich partition coefficients (K_f) (Hassett et al., 1980).

	K_f				
Sample	Fresh	Frozen	Air-dried	Freeze-dried	Oven-dried
Sangamon	1.07	1.07	0.95	0.95	0.84
Crane Island	0.90	0.99	1.04	1.09	1.09
Mean[a]	0.98	1.03	1.00	1.01	0.97

[a] Means were not significantly different at the 5% level

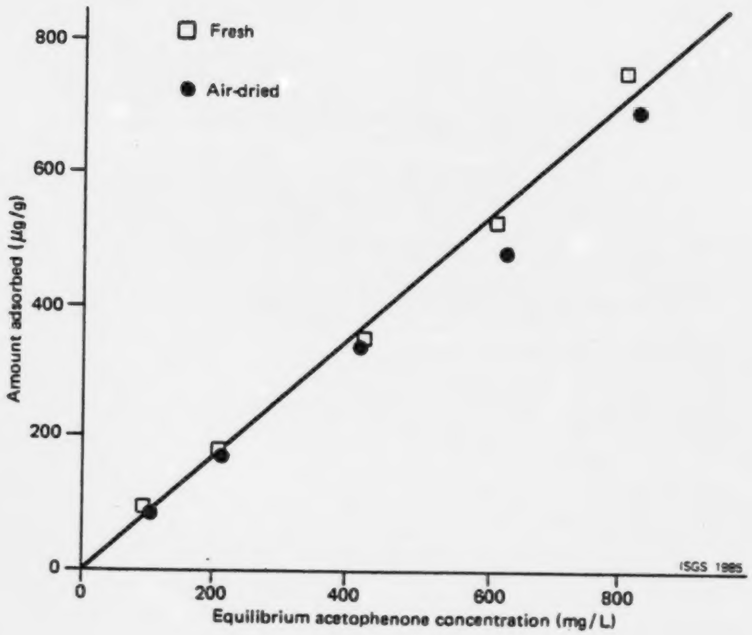

Figure 4. Adsorption isotherm of acetophenone by fresh field moist and air-dried samples of Crane Island alluvium (adapted from Hassett et al., 1980).

both the cation exchange capacity (CEC) and anion exchange capacity (AEC). Bar-Yosef et al. (1969) found that oven-drying kaolinite at 110°C reduced the amount of phosphate that could be desorbed relative to clay samples that were not heat-treated. They thought that possibly during drying the phosphate tetrahedra may have changed its stearic configuration to a form more conducive to bonding.

In summary, drying adsorbent samples in order to homogenize and store the samples until they are needed may influence the results obtained by batch adsorption studies. Bartlett and James (1980) concluded that either air-drying or oven-drying may be viable methods of sample preparation if the potential changes in adsorbent properties are understood and confronted. However, understanding and confronting these changes may be research projects in themselves.

- As a guideline for conducting batch adsorption studies, it would appear that the oven-drying of adsorbents is not an advisable technique to accelerate drying even though air-drying may take several days with large bulk samples. Air-drying samples in contact with the atmosphere minimizes any changes that may occur due to drying and is the most practical approach at this time. The American Society for Testing and Materials defined air-drying as a process of partial drying (of the sample) to bring its moisture content near equilibrium with the atmosphere in the room in which further reduction and division of the sample is to take place (ASTM, 1979). It appears advisable to keep air-drying to the minimum necessary to allow preparation of the sample, and to provide a stable condition for measurements of the sample such as weighing. Air-drying anaerobic soils and sediments will require special handling in order to prevent the relatively reduced materials from oxidizing if exposed to the atmosphere. Anaerobic materials can be "air-dried" in a glove box or in a glove bag that is supported by a continuous supply of dry oxygen-free nitrogen or argon gas.

SECTION 3: EFFECTS OF TEMPERATURE

Adsorption at the solid-liquid interface tends to occur when the attractive forces between the surface and ionic solutes are greater than those between the solutes and the solvent (Zettlemoyer and Micale, 1971). The adsorption of an ionic or polar solute is often the result of a thermodynamically favorable change in the enthalpy (ΔH) (Hassett et al., 1981) or sometimes by a favorable change in the entropy (ΔS) of the system where the $-T\Delta S$ term from the Gibbs-Helmholtz equation compensates for the positive value of ΔH (Thomas, 1961) where T is the temperature of the system. The adsorption of nonpolar organic solutes is thought to be primarily the result of a thermodynamically favorable change in entropy (ΔS) involving little energy transformation as heat. Thus it is valid to anticipate that the adsorption behavior of ionic or polar solutes will show some temperature dependency, whereas the adsorption of nonpolar solutes may not be greatly influenced by the temperature of the system. The direction and magnitude of temperature dependency will depend on the specific solute-soil system.

An early paper by Jurinak and Bauer (1956) reported that the adsorption of zinc by calcite was exothermic; the amount of zinc adsorbed decreased with increasing temperature. In contrast, Kuo and Mikkelsen (1979) studied the adsorption behavior of zinc by soils at temperatures ranging from 10°C to 35°C and found that the zinc adsorbed endothermically; increased adsorption was associated with higher temperatures.

Kinniburgh and Jackson (1981) reviewed the literature on cation adsorption by soils and concluded that the effects of temperature were usually small, but in some cases they significantly influenced adsorption data.

The adsorption of phosphate by soils and soil materials is often endothermic (Low and Black, 1950; Gardner and Jones, 1973; Griffin and

Jurinak, 1973a; Singh and Jones, 1977; Taylor and Ellis, 1978). The adsorption of arsenate was also found to be an endothermic reaction (Fig. 5). The amount of arsenate adsorbed in equilibrium with a solution concentration of 50 mg/L as total As at 15°C was about 31% (mass basis) less than that observed at 25°C and approximately 51% less than the amount adsorbed at 35°C.

In contrast to ionic species, Hassett et al. (1983) found that the adsorption of the nonpolar solutes phenanthrene and α-naphthol by soils was largely unaffected by temperature variations from 15°C to 35°C (Table 4). The adsorption of 1, 2-dichlorobenzene by a soil sample studied by Chiou et al. (1979) was insensitive to temperature differences between 3.5°C and 20°C, but the adsorption of 1,1,1-trichloromethane was reduced at the lower temperature.

Weber et al. (1983) found that the adsorption of Aroclor 1254 by a Saginaw River sediment was temperature-dependent; adsorption was reduced over a 10-degree temperature range. Moreover Voice (1986, written communication) demonstrated that the adsorption of 2,4,5,2',4',5'-hexadiclorobiphenyl by a Lake Michigan Sediment decreased with decreasing temperature over a 20-degree temperature range.

The effect of temperature on adsorption data is ultimately linked to the thermodynamics of the adsorption process. This relationship may be approximated by a Clausius-Clapeyron-type equation, integrated over a narrow temperature range, viz.,

$$R \ln(C_2/C_1)/(1/T_2-1/T_1) \approx \Delta H' \qquad [1]$$

where C_1 and C_2 are the equilibrium concentration of a solute at two different temperatures, T_1 and T_2, and $\Delta H'$ is the apparent heat of adsorption.

Apparent heats of adsorption values may be used as estimations of the amount of heat energy isothermally released or absorbed during the course of

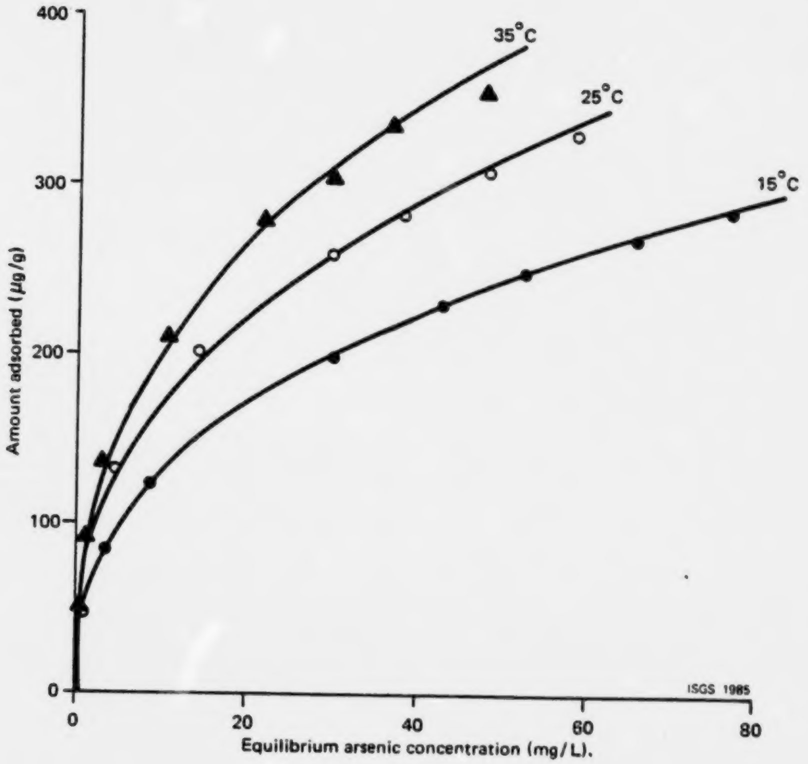

Figure 5. Arsenate adsorption isotherms by Catlin at 15°C, 25°C and 35°C, and at pH 6.6.

Table 4. Effect of temperature on Freundlich adsorption constants (K_f) for phenanthrene and α-naphthol (Hassett et al., 1983).

Solute	Soil	Freundlich constant (K_f)		
		15°C	25°C	35°C
phenanthrene	5	328	304	340
	15	117	151	126
α-Naphthol	5	5.4	5.5	7.7
	15	19	25	31

adsorption, although it is probably more correct to view such values as heats of the overall reaction. Eq. [1] can be rearranged as

$$\frac{C_2}{C_1} = \exp\left(\left(1/T_2 - 1/T_1\right) \Delta H^{\circ\prime}/R\right) \qquad [2]$$

Eq. [2] can be used to estimate the effects of temperature if $\Delta H^{\circ\prime}$ of the specific adsorbent-solute system is known. If the magnitude of $\Delta H^{\circ\prime}$ is small such as with the adsorption of some hydrophobic organic solutes, then the ratio of C_2 to C_1 will be close to 1. In other words, the solute concentration at temperature 1 will be nearly the same concentration as at temperature 2, given that all other conditions are the same; such results for some organic compounds are given by Hassett et al. (1983). In contrast, the adsorption of phosphate is often associated with relatively large $\Delta H^{\circ\prime}$ values. Consequently phosphate adsorption may be sensitive to ambient temperature fluctuations. Moreover, if the temperature fluctuations are large (the difference between T_1 and T_2 in eq. [2]), there is a greater potential for the equilibrium solute concentrations to be affected by temperature changes or fluctuations. To avoid this experimental artifact, adsorption experiments are usually conducted with temperature-controlled water baths or constant temperature rooms. If such facilities are not available or are impractical, it is suggested that the laboratory work be conducted in rooms where the ambient temperature fluctuates by no more than 6°C (i.e., 22 ± 3°C). This 6-degree range was based on the assumption that a "typical" heat of adsorption value for most solutes of environmental significance is approximately $<$ 20 kJoule/mole, based on the discussions in Section 1. This suggested range should be acceptable for most situations, but in cases where the adsorption of the solute results in a comparatively large heat of adsorption, more rigorous temperature control may have to be implemented.

- In summary, it is recommended that these batch adsorption procedures should be conducted under constant temperature conditions, if available, or in rooms where the ambient temperature is fairly constant (e.g., 22 ± 3°C). It is also recommended that when the batch experiments are performed, the temperature of the room should be recorded and treated as a potential variable that may influence the data or as one that may be useful in the interpretation of the results.

SECTION 4: STABILITY OF NONIONIC ORGANIC SOLUTES IN SOLUTION

In conducting a batch adsorption procedure, it is important to consider the physicochemical stability of the solute in solution. Processes such as photodegradation, hydrolysis, and/or microbial degradation can potentially contribute to a decrease in solute concentration concomitantly with adsorption, and these changes may even occur before the solution is contacted with the adsorbent.

1. Photolysis - Photoreactive solutes which absorb light at wavelengths greater than 290 nm may be subject to rapid photolysis in glass containers. For example, the half-life of hexachlorocyclopentadiene (C-56) was found to be less than 5 minutes when exposed to sunlight (Chou and Griffin, 1983). Therefore, it is recommended that precautions be taken to ensure that substances such as these are protected from light, not only sunlight but laboratory lights as well. Appropriate measures include use of amber glass, wrapping glassware in aluminum foil, or any other suitable technique that will eliminate the possiblity of photolysis transformations via exposure to light. A simple aqueous screening test is presented here to help determine the stability of the solute(s) in the presence of light. This procedure was designed to eliminate volatilization losses and ensure that only reductions in concentration due to photolysis are measured during the test.

Photolysis Test:

In this screening test, place the initial stock solution into either a 30-mL or 50-mL borosilicate glass hypo-vial and fill the vial to eliminate any head space. Then seal the vial with a teflon-faced septum and aluminum crimp-cap to prevent volatilization, and place replicate samples in sunlight for 2, 4, and 6 hours. Analyze duplicate samples of the unexposed solute to determine the concentration at time = 0 and in two freshly opened hypo-vials after 2, 4, and 6 hours of exposure, respectively. Also determine the concentration of the solute in each of two control vials (wrapped with aluminum foil or in amber glass vials) that have also been similarly exposed as the samples. Select an analytical method which is most applicable to the analysis of the specific solute under study. Chromatographic methods are generally recommended because of their chemical specificity in analyzing the parent compounds without interference from impurities. If the results indicate the solute is photoreactive, then all subsequent tests and adsorption studies must be conducted under conditions which prevent exposure to light during the reactions and analytical steps.

2. Hydrolysis - Hydrolysis is an important degradation path for certain classes of nonionic solutes, and it is necessary to know whether the solute under study is subject to hydrolysis during the period of the adsorption study. Otherwise, the amount of solute adsorbed by soils or sediments could be over-estimated if changes in solution concentration due to hydrolysis are not taken into account. Details of the hydrolysis reactions of various types of compounds can be found in many kinetics texts (e.g., Laidler 1965, Frost and Pearson 1961). Discussions of hydrolysis from an environmental point of view have also been published (Mabey and Mill 1978, Tinsley 1979).

It is important that the temperature of a hydrolysis screening test procedure be kept constant. The temperature used in the hydrolysis test procedure should be the same temperature to be used in the adsorption experiments. The pH is also important and it is recommended that the hydrolysis screening test be carried out at the same pH range that will be used in the adsorption studies. The prevention of photolysis is to be implemented as previously discussed. In some cases, the hydrolysis of solutes may be enhanced by the presence of other substances such as iron which catalyzed the rate of hexachlorocyclopentadiene hydrolysis under conditions of low pH (Chou and Griffin, 1983). Therefore, the composition of the test solution must be considered.

Hydrolysis Screening Test:

Fill either a 30-mL or 50-mL Hypo-vial completely with the test solution to eliminate any head space, then seal the vial with a teflon-faced septum and aluminum crimp-cap. Place replicate samples in a constant temperature room or water bath for 6, 12, 24, and 48 hours. Select an analytical method which is most applicable to the analysis of the specific compound under study and analyze duplicate samples of the concentration of the chemical substance at time = 0 (control), and in two, freshly opened Hypo-vials after 6, 12, 24, and 48 hours.

If significant hydrolysis is indicated by the results of this test, this must be considered in the interpretation of results from adsorption studies and special care should be given to the handling of flasks and to the analytical steps employed.

3. Microbial Degradation

Microbial degradation can also decrease the solution concentration of the solute thus leading to an overestimation of the amount adsorbed by the adsorbent. Therefore, for easily degraded (labile) compounds, a batch technique will measure "apparent adsorption," which is in reality a combination of adsorption and degradation (and hydrolysis as indicated by the results of test 2). The influence of microbial degradation on "apparent adsorption" of phenol by soil was studied by Scott et al. (1982). They found that Freundlich K_f values for the adsorption of phenol by nonsterile soil increased linearly with time with a Palouse silt loam and increased exponentially with time with

Captina silt loam. The Freundlich K_f values associated with adsorption by sterile soils remained essentially constant after 8 hours. A similar study for p-cresol was also reported by Boyd and King (1984). Their data indicated that under aerobic conditions, p-cresol degradation was initiated within 10 hours, and complete degradation occurred within 48 hours or less for initial p-cresol concentrations of 5, 10, 20, and 50 μg/L. The adsorption of organic compounds, such as phenol or other labile organics which are degraded within the time required to attain adsorption equilibrium, cannot be evaluated accurately without accounting for or eliminating microbial degradation losses.

Biodegradation Screening Test:

The most common approach used to screen whether an adsorbate undergoes biodegradation is to conduct kinetic studies by using sterile and non-sterile soil. Prior to the kinetic studies, the weighed soil is placed into a reaction bottle and then autoclaved three times at 2-day intervals, each time for 2 hours at 120°C and at 1.4 bar pressure (Scott et al., 1982). (See the Section on Effects of Adsorbent Preparation to help evaluate the possible changes in adsorbent characteristics caused by autoclaving.)

Bulk solutions of the solute are prepared in distilled water and passed through a sterilized 0.22-μm membrane to sterilize the solutions, then known amounts of the solutions are transferred to the sterilized and non-sterilized reaction bottles and sealed with sterilized teflon-faced septa and aluminum crimp-caps. All samples are equilibrated at constant temperature for 4, 8, 16, 24, and 48 hours. At the end of each equilibration period, the solid phase soil particles are separated from the solution phase by centrifuging duplicate reaction bottles at 2,000 rpm for 1 hour. Aliquots of the supernatant solution are taken with a syringe through a hole and septum in the caps of the bottles. Select an analytical method which is most applicable to the analysis of the specific solute under study. The major purpose of the suggested test procedure is only for screening for biodegradability.

If the test indicates the solute to be biodegradable to a significant extent during the period of the adsorption test, then the reaction times or temperatures may have to be modified to reflect this result. The results of the adsorption study must then be interpreted in the context of the solute equilibration time and the environmental significance of the biodegradation of the solute relative to its adsorption affinity for soil materials.

SECTION 5: EFFECTS OF SOLUTION pH

The adsorption behavior of ionic and ionizable inorganic and organic solutes by soils and soil materials is often influenced by the pH of the soil-water system. In general, the adsorption of inorganic cations increases with increasing pH (Kinniburgh and Jackson, 1981). For example, Griffin and Shimp (1976) reported that the amount of lead adsorbed by kaolinite from a landfill leachate was pH-dependent; the amount of lead removed from solution increased with increasing pH. In their batch adsorption experiments, as with similar studies, the pH of the soil solutions was periodically adjusted to the indicated pH by the addition of either dilute acids or bases. A sharp change in slope of the isotherms between pH 4 and 6 was attributed to the precipitation of $PbCO_3$. The reduced adsorption at the lower pH values was attributed to the increase in competition for adsorption sites by H^+ and by Al^{3+} resulting from the dissolution of the clay. Similar examples for Cd, Cu, and Zn (Fig. 6) show that higher pH values have been associated with greater removal from solution. Relatively small differences in pH (~ one-half of a pH unit) can result in major differences in the amount of solute adsorbed.

The pH of the soil solution has also been shown to have a direct effect on the adsorption of anionic solutes. In contrast to cationic solutes, anion adsorption is generally enhanced in acidic environments, however, some anionic solutes are adsorbed to a greater extent in alkaline systems. Parfitt (1978) generalized that sulfate adsorption by soils becomes essentially insignificant above pH 8, while the adsorption maxima of boric acid and silicic acid appears to correspond to a pH of approximately 9. White (1980) generalized that phosphate adsorption by goethite decreased uniformally between pH 3 and 12, while the magnitude of phosphate adsorption by alumina passes through a maximum value between pH 4 and 5. Griffin et al. (1977a) found that the

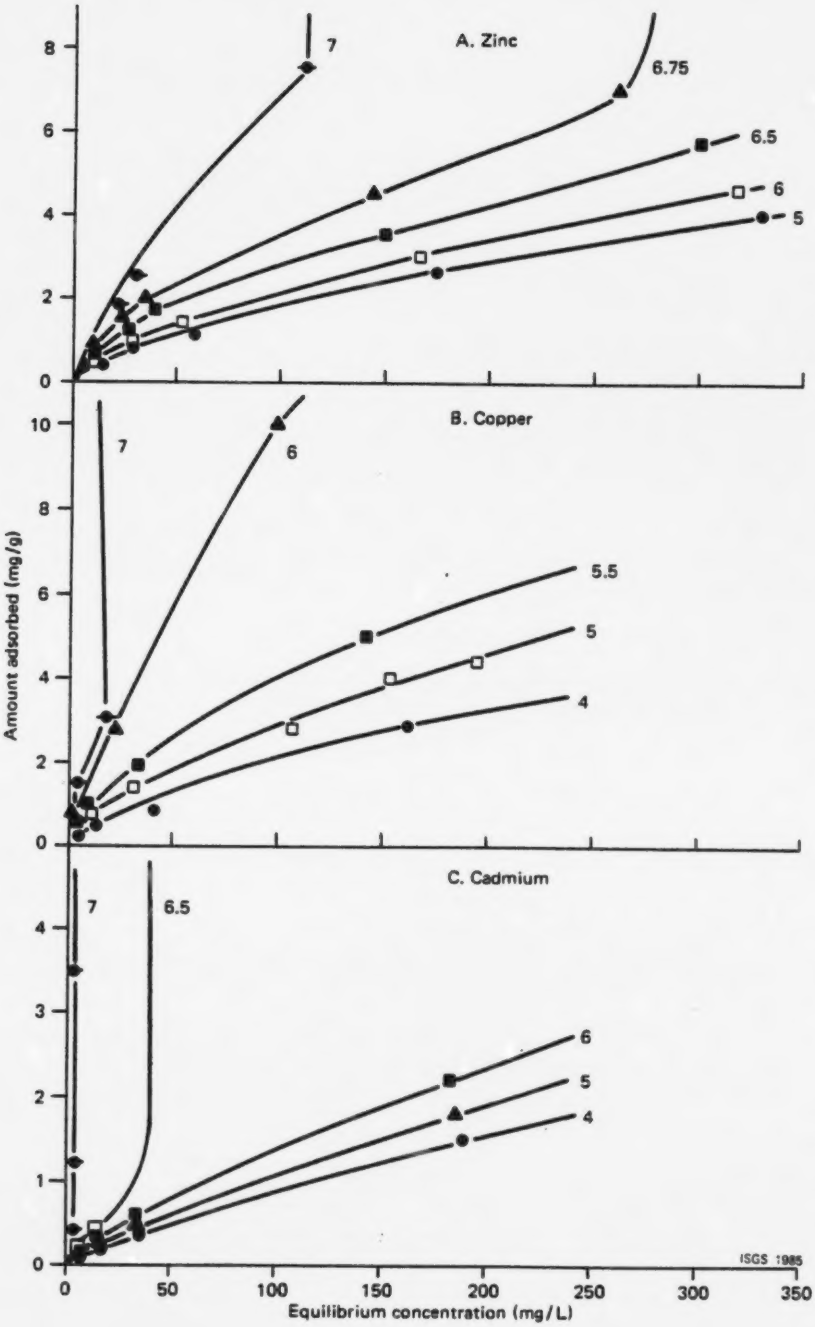

Figure 6. Zinc, copper, and cadmium adsorption from a DuPage County landfill leachate by kaolinite at 25°C at various pH levels (Frost and Griffin, 1977)

adsorption of chromium (VI) at low concentrations by kaolinite passed through a maximum value between pH 4 and 5 (Fig. 7). No adsorption occurred above pH 8.5.

The adsorption of arsenic as arsenate (As(V)) is also pH-dependent with lower pHs resulting in greater adsorption (Fig. 8). The adsorption of molybdate by soils also appears to exhibit a maximum value at pH 4 (Parfitt, 1978). This trend, characteristic of most inorganic oxyanions, is thought to be the result of the increased positive charge due to the increased protonation of surface hydroxyls associated with the edges of colloidal particles and hydrous metal oxides in acidic environments. The adsorption behavior of arsenic as arsenite (As(III)) may (Griffin et al., 1977b) or may not (Pierce and Moore, 1982, Fig. 8 of this report) be strongly dependent on pH.

The adsorption of ionizable organic solutes is also influenced by the pH of the soil solution. For example, Frissel and Bolt (1962), Weber (1966), and Hance (1969) showed that the adsorption of the triazine increased as the pH decreased (Fig. 9). At low pHs, the triazine solutes may have been increasingly protonated, which increased the magnitude of coulombic interaction with negatively charged sites on clay surfaces. McGlamery and Slife (1966) found that the adsorption of atrazine by the Drummer clay loam was influenced more by pH than by temperature.

Frissel and Bolt (1962) also presented data illustrating the pH-dependency of the adsorption of other ionizable organic compounds (the herbicides MCPA, 2,4-D, DNBP, and 2,4,5-T) by clays. The adsorption of DNBP (Fig. 10), for example, sharply decreased as the pH of the system increased from approximately pH 4.7 to pH 6. In alkaline solutions (pH > 7), DNBP adsorption was reduced due to negative adsorption which occurred, i.e., the DNBP was repelled by the clay. In this pH range, DNBP occurred largely as neutral molecules since the pK of the organic solute was 4.35. The adsorption

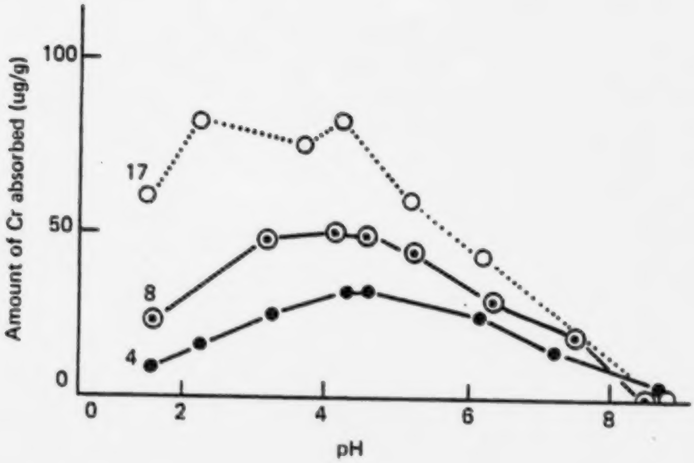

Figure 7. Chromium (VI) adsorption by kaolinite at 25°C at various pH levels. The chromium concentrations shown are the initial concentrations added (modified from Griffin et al., 1977a).

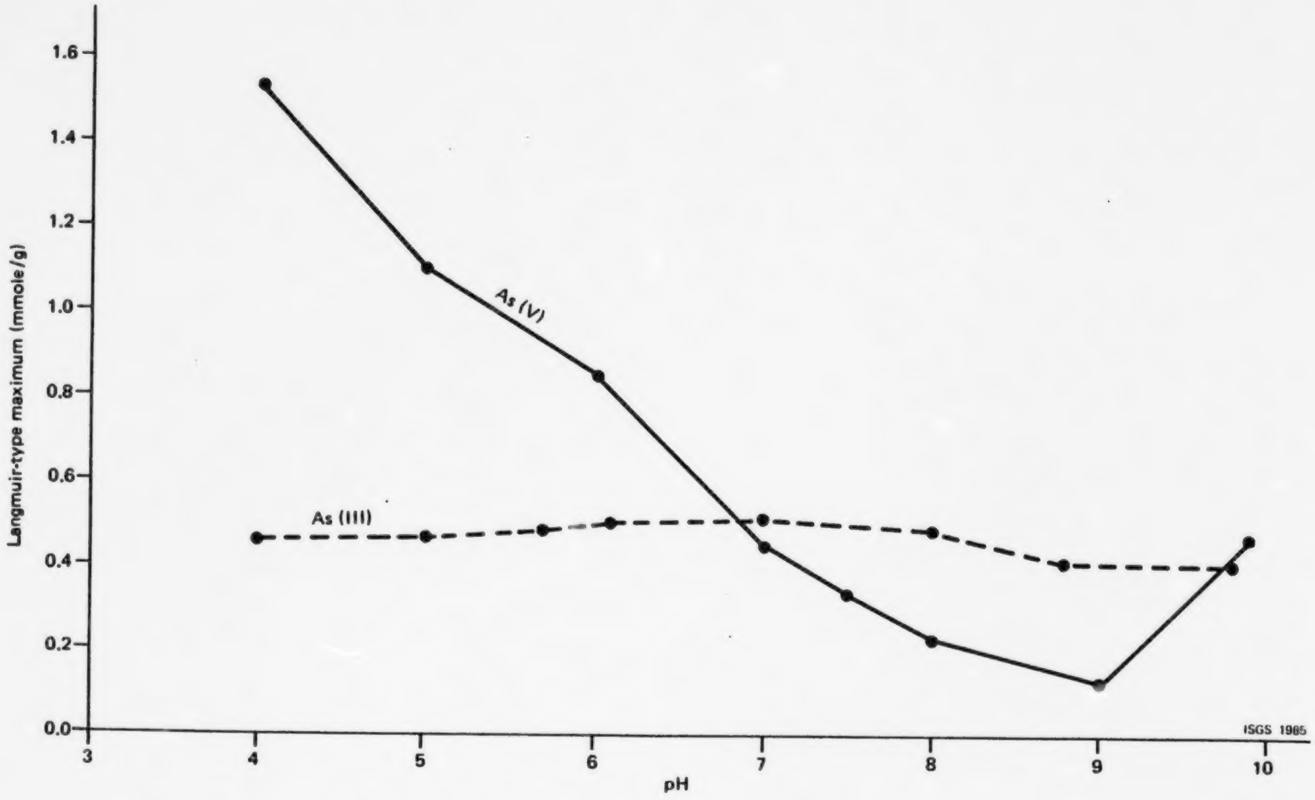

Figure 8. Langmuir-type maximum (mM/g) for the adsorption of arsenic as As(V) and As(III) by amorphous iron hydroxide (Pierce and Moore, 1982).

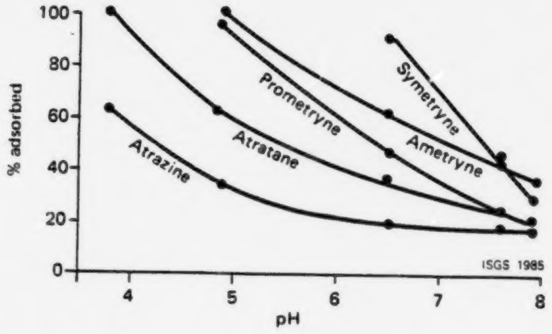

Figure 9. Effect of pH on the adsorption of triazines by a Ca-montmorillonite sample (adapted from Hance, 1969).

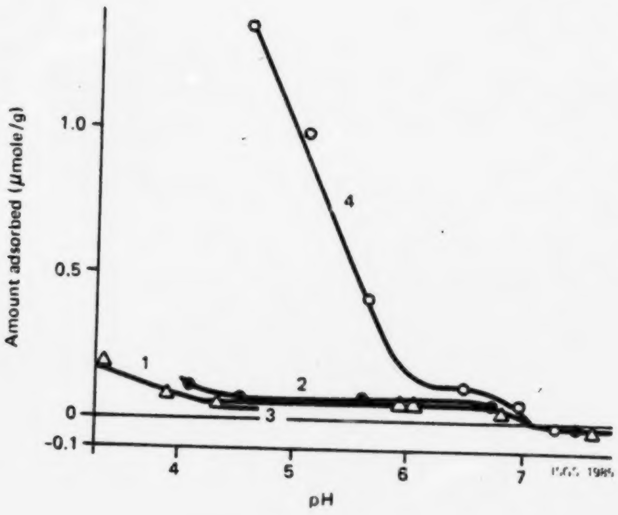

Figure 10. Effect of pH on the adsorption of different ionizable organic solutes by an illite sample (1) 2,4-D, (2) 2,4,5-T, (3) MCPA, and (4) DNBP (adapted from Frissel and Bolt, 1962).

of benzidine also followed a similar pattern. The ionization constants of benzidine are 4.3 and 3.3 (pKb_1 and pKb_2, respectively). Consequently, Zierath et al. (1980) found that the amount of benzidine adsorbed by two soils decreased when the solution pH was increased from a pH of 5 to pH 11. Benzidine can exist in solution as both ionized (cationic) species and a neutral species. As the pH of the suspensions was increased, a larger portion of the total amount of benzidine existed as the neutral form. Both species are subject to adsorption, although the cationic form should be adsorbed to a much greater extent due to Coulombic interactions.

The adsorption behavior of neutral, nonpolar hydrophobic organic solutes appears to be largely unaffected by the pH of the soil-water system. Hassett et al. (1980) found no correlation between the adsorption behavior of polycyclic aromatic hydrocarbons (PAH) and the pHs of 14 soils ranging from pH 4.5 to 8.3. Correlations between the adsorption constants and the actual pH of the solutions were not attempted. In the present study, the adsorption of the PCB Aroclor 1242 was not significantly influenced by the pH of three different soil suspensions (Fig. 11). The linear Freundlich constants (Kd) were essentially constant over the range of pH 3 to approximately 10.

- In summary, the potential influence of pH on the results generated by batch adsorption procedures will depend on the system under study. It is recommended that the equilibrium pH of the soil-solute mixtures be determined prior to separating the solution from the soil or soil component suspension and routinely given along with the adsorption data. In the case of anaerobic adsorbent-solute systems, pH measurements should be conducted in a glove box or bag so that the suspensions do not oxidize when the containers are opened. The failure to measure and report pH data may render the adsorption data impossible to interpret in a meaningful way.

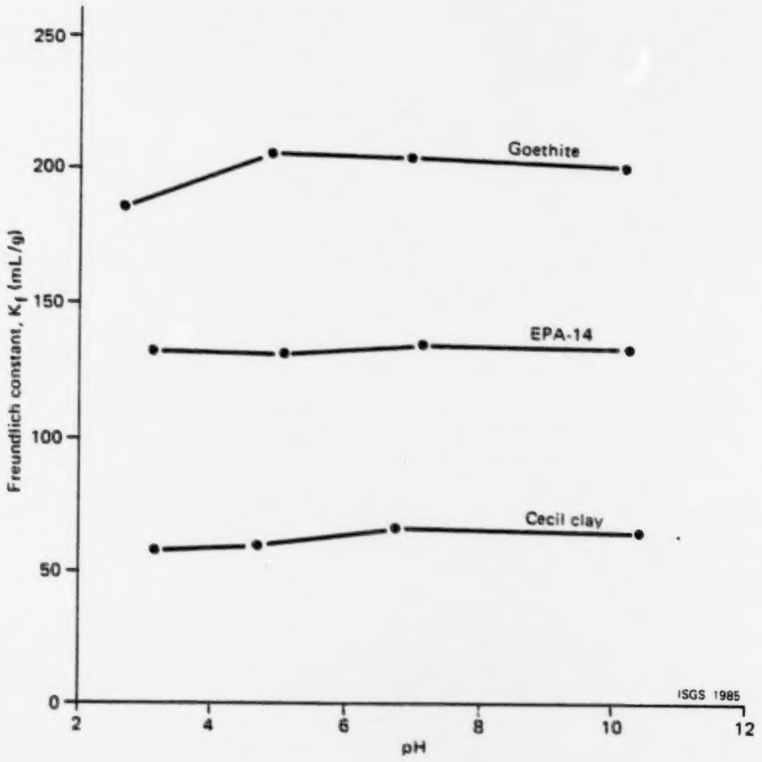

Figure 11. The adsorption behavior of the PCB Aroclor 1242 by a synthetic goethite, a Cecil clay, and EPA-14 soil samples as a function of pH at 24°C.

SECTION 6: EFFECTS OF IONIC STRENGTH

The ionic strength of the solution in batch adsorption procedures may have several direct and indirect effects on the results. The extent of these effects will depend on both the magnitude of the ionic strength and on the concentration, composition, and charge of the ionic constituents constituting the ionic strength of the adsorbent-liquid system.

Without regard to the specific composition of the solution, the ionic strength may directly affect batch adsorption data in two ways: 1) changes in solute activity, and 2) changes in the thickness (and therefore properties) of the diffuse electrical double layers associated with colloidal particles. The activity of most solutes tends to decrease as the ionic strength of the solution increases due to the shielding effect arising from neighboring ions. However, beyond a threshold ionic strength (often in very concentrated solutions such as brines), the activity of some ionic constituents reverses itself and steadily increases, finally yielding activities exceeding their original concentration (Fig. 12). This phenomenon is relevant to batch adsorption data since the use of actual solute concentrations rather than activities of ions may not yield calculated results that agree with observed results due to the departure of concentration from ideality in non-dilute systems. Discussion of this topic may be found elsewhere (Atkins, 1982; Bohn et al., 1979; Bolt and Bruggenwert, 1978; Garrels and Christ, 1965; and Stumm and Morgan, 1981).

It is a basic tenet of Diffuse Double Layer Theory that the physical thickness of the electrical double layer composed of adsorbed cations about a colloidal particle is inversely proportional to the ionic strength of the bulk solution. This phenomenon may not only affect exchange and adsorption reactions at the solid-liquid interface, but may control the physicochemical

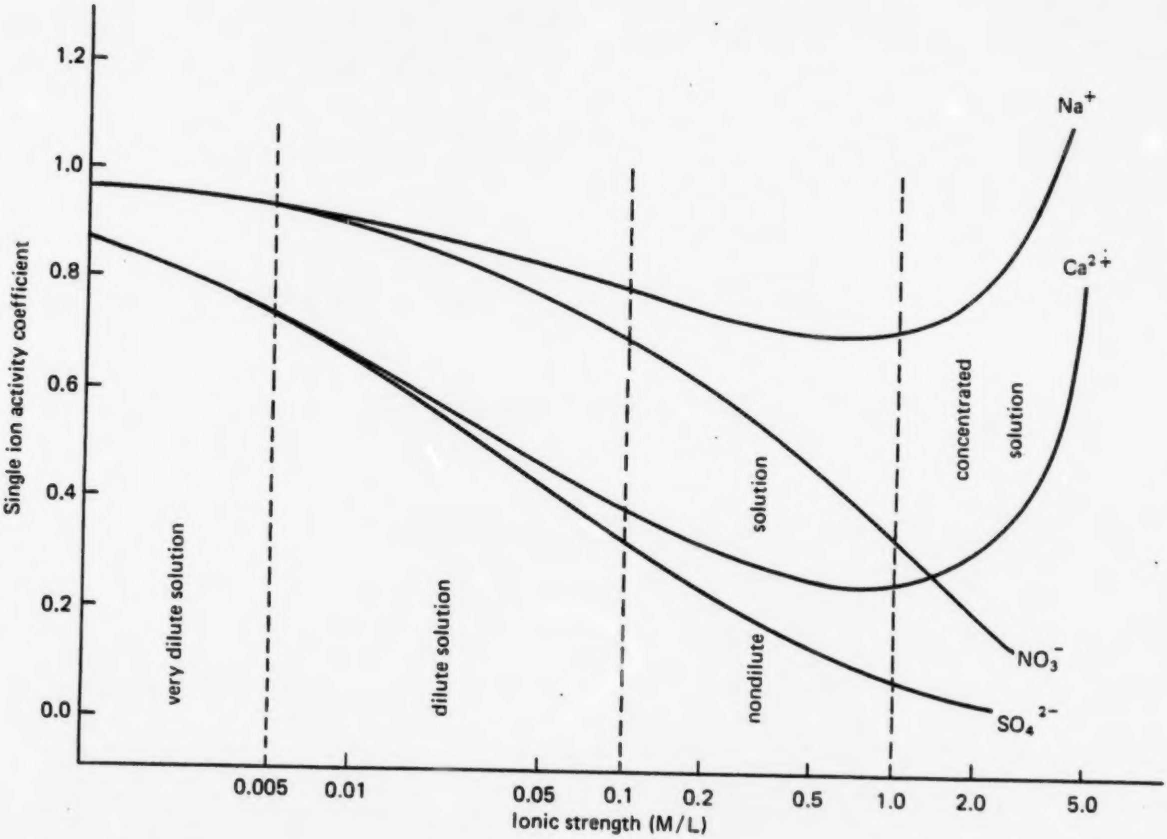

Figure 12. Ratio of concentration to activity (i.e., single ion activity coefficient) versus ionic strength for some common ions.

properties of the material at the macroscopic level, such as hydraulic conductivity.

In attempts to minimize changes in ionic strength in the construction of adsorption isotherms, some investigators added a water soluble compound to serve as a background electrolyte (sometimes referred to as a support medium or background ionic medium) to the solutions containing the solute(s) under study. The selection of background electrolytes and concentration has varied considerably, and the rationale for the choice has rarely been explained or justified (Ryden and Syers, 1975).

The addition of a background electrolyte has been observed to have no measureable effect in some soil-solute systems while both synergistic and antagonistic effects have been observed in other systems. The effect of ionic strength on phosphate adsorption has received much attention. Helyar et al. (1976) concluded that phosphate adsorption by gibbsite was independent of ionic strength in the range of 0.002 M to 0.02 M when the ionic strength was controlled by NaCl, KCl, and $MgCl_2$. However, Ryden and Syers (1975) and Ryden et al. (1977) reported that phosphate adsorption by two soils in a 40-hour interval increased as the ionic strength of the solutions was increased by the addition of 10^{-3} M to 1 M NaCl. The adsorption of selenite by goethite was reported by Hingston et al. (1968) as being insensitive to ionic strength in the range of 0.01 M to 1.0 M.

Common to many studies is the observation that polyvalent cation salts promote phosphate adsorption relative to that from distilled water (Barrow, 1972; Fox and Searle, 1978; Heylar et al., 1976; El Mahi and Mustafa, 1980; and White, 1980). Helyar et al. (1976) speculated that Ca^{2+} may act as a potential determining ion while others (El Mahi and Mustafa, 1980) suspected that the solubility of solid phosphate compounds was exceeded (see also Anderson et al., 1981).

The relationship between ionic strength and the adsorption of organic solutes has also been examined. Increasing the ionic strength from less than 0.01 to 0.1 N resulted in a significant increase in adsorption of 2,4,5-T (Koskinen and Cheng, 1983). This trend has been observed with other weakly acidic herbicides, such as picloram (4-amino-3,5,6-trichloropicolinic acid) (Farmer and Aochi, 1974) and 2,4-D (2,4-dichlorophenoxyacetic acid) (Moreale and Van Bladel, 1980). The increase in adsorption of the weakly acidic herbicides cited here was attributed to a decrease in pH. A decrease in pH would increase the proportion of the molecular species, which could then be adsorbed. On the other hand, Choi and Aomine (1974) found that increasing the ionic strength at constant pH decreased the adsorption of pentachlorophenol (a weak acid: $pK_a = 4.5$), and the amount of decrease was dependent on the anion used in adjusting the ionic strength of the solution containing the pentachlorophenol. In batch adsorption studies, Abernathy and Davidson (1971) found that the adsorption of fluometuron (1,1-dimethyl-3-(a,a,a-trifluoro-m-tolyl)urea) was decreased and prometryn (2,4-bis(isopropylamino)-6-(methylthio)-s-triazine was increased by increasing the $CaCl_2$ concentration from 0.01 to 0.5N.

In experiments designed to evaluate the effect of solution ionic strength on 2,4,5,2',4',5'-hexachlorobiphenyl (HCBP) adsorption, Horzempa and DiToro (1983) found that the Freundlich constant (K_f) appeared to be only slightly influenced by increasing NaCl concentration from 10^{-4} M to 10^{-2} M. However, in similar experiments $CaCl_2$ significantly affected the K_f values over the same concentration range.

The use of background electrolytes may also promote competitive interactions between the ions derived from the background electrolyte and the solute(s) under study. (Competitive interactions are discussed in Section

11.) For example, Griffin and Au (1977) found that the adsorption of Pb by montmorillonite was reduced when 0.1 M $Ca(ClO_4)_2$ was used as a background electrolyte. The excess Ca^{2+} in solution was also adsorbed by the clay reducing the number of adsorption sites available to Pb relative to that in a distilled water system. Other "side reactions" may take place that can complicate batch adsorption data; Na-Ca and Na-Mg exchange reactions on bentonite were unaffected by ClO_4^- in a study by Sposito et al. (1983) while Cl^- appeared to become a reactant in the exchange reactions, rather than serving as an "inert" background electrolyte. The formation of $CaCl^+$ and $MgCl^+$ complexes may have caused the observed exchange behavior.

The appropriateness of the use of a background electrolyte depends on three factors:

1. the specific conceptual model of the adsorbent-solute system envisioned by the investigator,
2. the chemical nature of the system itself, and
3. the overall objectives of the investigation and the intended use of the data.

The position taken in developing the batch adsorption procedures presented in this document was governed by the philosophy that they should be simple and designed primarily for routine use. Thus the use of a background electrolyte was rejected in anticipation that the inherent ionic strength of the solutions will be influenced by the chemical constituents occurring in the leachate or extract, and those derived from soluble constituents in the particular clay or soil under investigation.

- It is recommended that the electrical conductivity (EC) of the equilibrated soil-solution be measured so that the ionic strength of the solution can be calculated by the relationship given by Griffin and Jurinak (1973b), viz.,

$$I = 0.0127 \times EC(dS/m) \qquad [3]$$

where I is the ionic strength in units of moles/L. In the case of anaerobic adsorbent-solute systems, EC measurements should be conducted in a glove box or bag so that the suspensions do not oxidize when the containers are opened. The failure to measure and report EC data and/or ionic strength may render the adsorption data difficult to interpret.

SECTION 7: EFFECTS OF PHASE SEPARATION

In a search of the literature, very few researchers were found to have used a filtration technique to separate the liquid and solid phases prior to the analysis of the liquid phase in batch adsorption studies. This is probably due to the potential of the filter membranes to retain significant quantities of the solute, particularly organic compounds. Luh and Baker (1970) found that a correction factor was necessary to account for retention of ^{14}C-tagged materials on the filters used in their study. The factor was reasonably constant, but the filtration technique was abandoned in favor of a centrifugation technique which avoided the problem by using gravitational forces to separate the solids from the liquid phase. In a preliminary test, Yaron and Saltzman (1972) also abandoned the filtration technique due to the filter paper retaining parathion. In similar studies, Griffin and Chou (1980) found that cellulose acetate membranes (0.45- and 0.22-μm pore size) adsorbed significant amounts of polybrominated biphenyls (PBBs) or hexachlorobenzene (HCB). The problem could be overcome but required a tedious presaturation technique. They showed that continuously passing nine 100-mL portions of HCB-saturated water through the membranes saturated the adsorption sites and yielded constant and reproducible values for the concentration of the compound passing through the membranes (Fig. 13). Figure 13 also indicated that presaturation of the membranes by soaking in HCB-saturated water yielded results that were not significantly different from results obtained by passing solution through the membrane.

The effects of centrifugation and filtration on arsenic concentrations were investigated (Fig. 14). In this case, there were no significant differences between filtration and centrifugation with respect to solute concentrations. It was concluded that laboratories performing adsorption

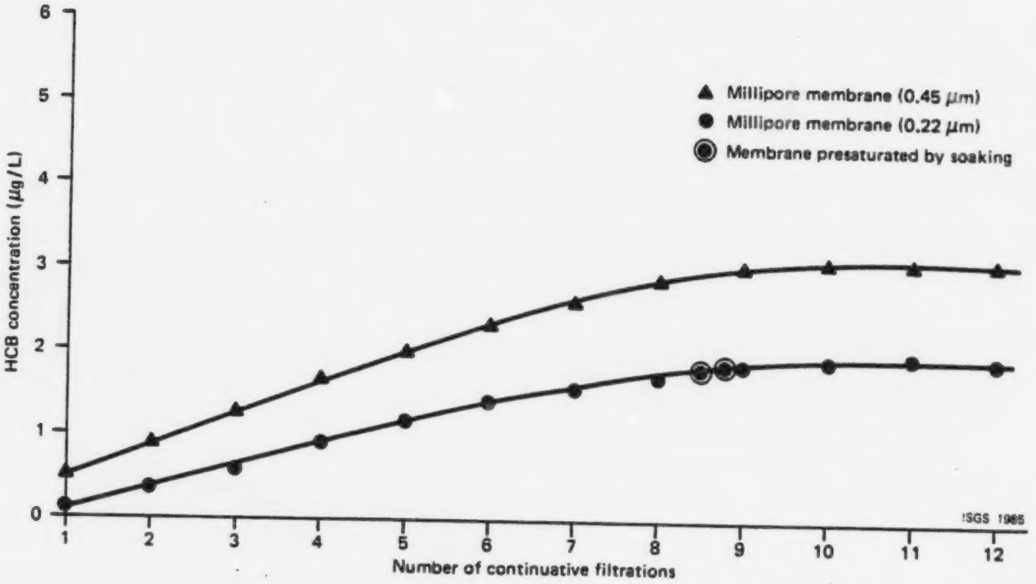

Figure 13. Effect of pore size and number of continuative filtrations of 100-mL aliquots of HCB-saturated water on the concentration of HCB in filtrates (Griffin and Chou, 1980).

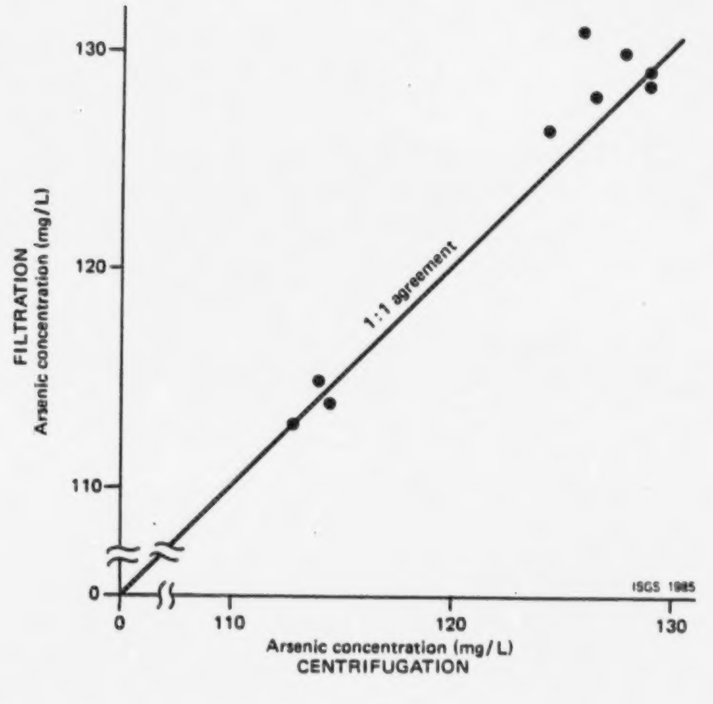

Figure 14. Distribution of arsenic concentrations in solutions that were either centrifuged or filtered. Values obtained by the two methods were statistically not significantly different (adapted from Griffin et al., 1985).

studies could be given the option of either filtration or centrifugation without impairing the general usefulness of the results as long as the affinity of the filtration membrane for the solute was evaluated adequately; failure to do so may lead to erroneous results.

- As a guideline for conducting batch adsorption studies, it is recommended that the solid and liquid phases be separated by centrifugation unless the investigator can clearly demonstrate that the use of filtration techniques does not significantly affect the results.

SECTION 8: EFFECTS OF THE METHOD OF MIXING

In theory, the equilibrium distribution of solutes and adsorbates should be independent of the mechanical device used to mix the solid-liquid mixture during the equilibration interval. However, there have been some indications in past studies that the method of mixing can influence the resulting adsorption data. For example, Barrow and Shaw (1979) compared three mixing methods in a study concerned with phosphate adsorption: a reciprocating shaker, a rotating tumbler, and a roller. They found that the amount of phosphate adsorbed was greatest when a reciprocating shaker was used, and phospate adsorption tended to be less when a roller was used to mix the suspensions. Barrow and Shaw (1979) felt that this trend was an experimental artifact, related to the vigor of mixing. They envisioned that the differences were due to particle breakdown; the more vigorous the agitation, the greater the soil particles were broken down exposing "new" adsorption sites available to phosphate for adsorption. They also acknowledged that the efficacy of the three agitation devices, with respect to their ability to thoroughly mix the suspensions, may have contributed to the differences.

In the development of the ASTM 24-hour Batch-Type Distribution Ratio (R_d) procedure described by Griffin et al. (1985), a first generation procedure was formulated around the ASTM-A, Water Shake Extraction Method (ASTM, 1979). A round-robin sensitivity analysis of this early procedure performed by a number of participating laboratories (see Acknowledgments) found that the method of mixing influenced the amount of cadmium and arsenic adsorbed by a Catlin silt loam sample; when shaking was more vigorous, greater amounts of solute were adsorbed. The results from the first sensitivity analysis are reported in Table 5. Large differences in concentrations between the laboratories yielded

Table 5. Results of first ASTM sensitivity analysis for cadmium (Cd) and arsenic (As) at high (200µg/mL) and low (10 µg/mL) initial concentrations where shakers and a paddle stirrer were used as the mixing method.

		High		Low		Shaker Rate	
		Cd	As	Cd	As	Strokes/min	Throw (inches)
Lab	Sample	µg/mL[a]					
A	1	16.87		0.080		59	3"
	2	13.24		0.034			
	3	11.36		0.022			
B	1	83.8	186	0.166	7.92	70	1.5"
	2	88.2	186	0.159	7.77		
	3	86.7	185	0.176	7.91		
C	1	1.88	128	<0.01	0.43	100	1.25"
	2	1.77	131	<0.01	0.38		
	3	1.70	127	<0.01	0.46		
C	1	26.5	162	0.064	5.00	70	1.25"
	2	21.5	168	0.057	4.78		
	3	10.0	175	0.096	5.81		
D	1	3.2		<0.01		Paddle stirrer used	
	2	3.2		<0.01			
	3	2.9		<0.01			
E	1	2.7	130	0.007	0.53	Not known	
	2	2.9	134	0.008	0.55		
	3	2.7	130	0.008	0.55		
Overall mean		21.2	153.5	0.073[b]	3.51		
S		30.8	25.6	0.064	3.32		
C.V.(%)		145.4	16.7	87.7	94.5		

[a] Represents post-procedure solute concentrations.

[b] Does not include values less than the detection limit.

interlaboratory coefficients of variation (% C.V.) in excess of 145 percent. This first round of interlaboratory study was a clear example of why a standard adsorption procedure was needed.

To improve the consistency of interlaboratory results, a National Bureau of Standards (NBS) rotary extractor was tested as the mixing system (Fig. 15). A second sensitivity analysis was carried out (Tables 6 and 7) where

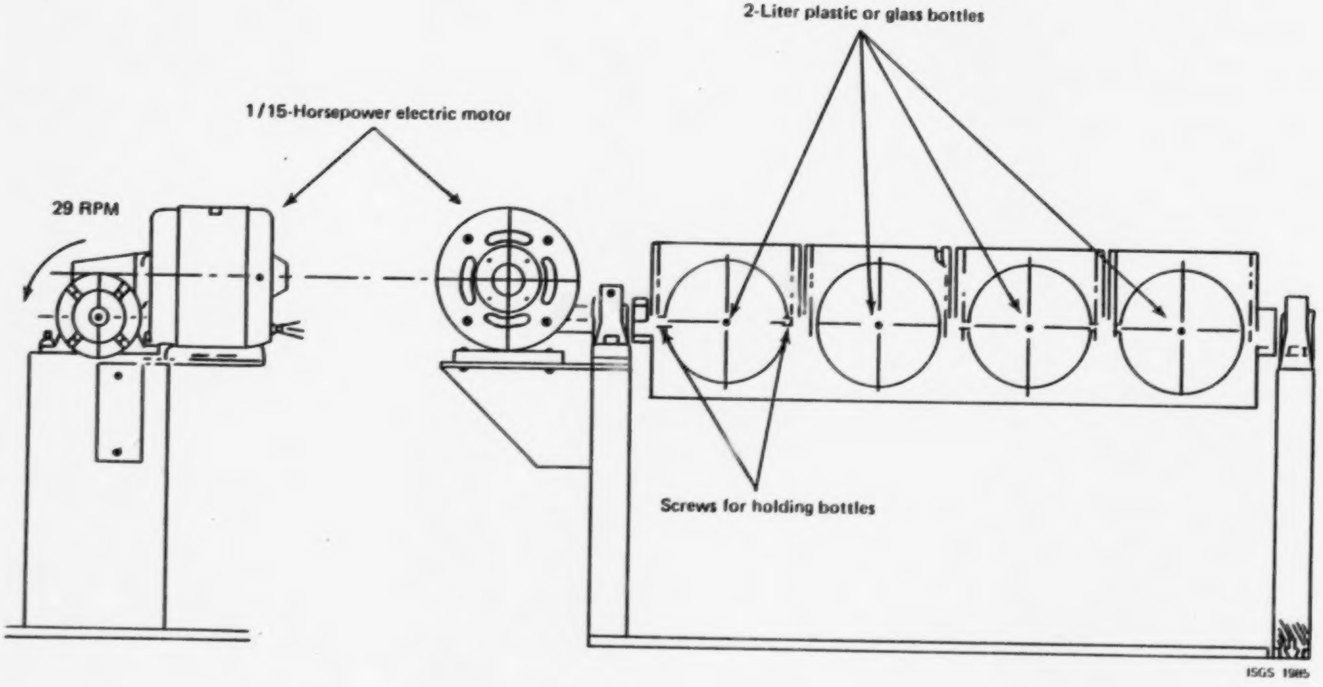
2-Liter plastic or glass bottles
1/15-Horsepower electric motor
29 RPM
Screws for holding bottles
ISGS 1985

Figure 15. The National Bureau of Standards Rotary Extractor (Diamondstone et al., 1982).

Table 6. Cadmium adsorption data from the 2nd ASTM interlaboratory sensitivity analysis using a NBS rotary extractor as the mixing method.

Lab	Initial conc.	24 hr conc.	R_d	Initial conc.	24 hr conc.	R_d
	- µg/mL	-	mL/g	- µg/mL	-	mL/g
A. Rep						
1	200	35.7	92.0	10.1	0.114	1734
2	200	36.2	90.5	10.1	0.126	1567
3	200	34.6	95.6	10.1	0.125	1580
B.						
1	200	31.8	105.8	10.0	0.110	1798
2	200	35.8	91.7	10.0	0.135	1461
3	200	36.8	88.7	10.0	0.165	1214
C.						
1	200	35.6	92.4	10.0	0.127	1554
2	200	35.6	92.4	10.0	0.127	1554
3	200	35.0	94.3	10.0	0.132	1495
D.						
1	190	31.0	102.5	9.8	0.130	1487
2	190	30.0	106.6	9.8	0.110	1761
3	190	31.0	102.5	9.8	0.120	1613
	$\bar{X}$	34.1	96.3		0.127	1568
	S	±2.3	±5.2		±0.01	±156
	C.V. (%)	7.1	6.6		7.94	9.97

Table 7. Arsenic adsorption data from the 2nd ASTM interlaboratory sensitivity analysis using a NBS rotary extractor as the mixing method.

Lab	Initial conc.	24 hr conc.	R_d	Initial conc.	24 hr conc.	R_d
	- µg/mL	-	mL/g	- µg/mL	-	mL/g
A. Rep						
1	205	180.3	2.74	10.0	5.76	14.72
2	205	180.3	2.74	10.0	5.85	14.18
3	205	182.0	2.53	10.0	5.89	13.95
B.						
1	200	175.5	2.79	10.0	5.52	16.23
2	200	178.0	2.47	10.0	5.40	17.03
3	200	170.7	3.43	10.0	5.48	16.49
C.						
1	200	186.3	1.47	10.0	5.57	15.90
2	200	177.3	2.56	10.0	5.64	15.29
3	200	175.0	2.85	10.0	5.59	15.77
D.						
1	200	160.0	5.0	12.0	6.80	15.29
2	200	180.0	2.22	12.0	6.80	15.29
3	200	180.0	2.22	12.0	6.90	14.78
	$\bar{X}$	177.1	2.75		5.93	15.42
	S	±6.65	±0.85		±0.56	±0.92
	C.V.(%)	3.76	30.9		9.47	5.99

each of the participating laboratories used an NBS rotating extractor. The coefficient of variation (% C.V.) between the mean values for each laboratory reflects in part the precision of the mixing method. The coefficient of variation of R_d values based on initial cadmium and arsenic concentrations of 10 mg/L and 200 mg/L were less than 8 percent and 12 percent for cadmium and arsenic, respectively. These results can be compared with those from the first round using predominantly shakers, which were as great as 145 percent for similar concentrations (Table 5). Because all other parts of the procedure were the same in both cases, the mixing method was concluded to be a primary contributor to the variation between the interlaboratory means. The NBS rotary extractor was adopted as the method of choice because of the much lower coefficient of variation between laboratory means.

- It is strongly recommended that all adsorption experiments, including both inorganic and organic systems, use an NBS rotary extractor or equivalent during each phase of the construction of an adsorption curve (i.e., determining a soil:solution ratio (Section 9), equilibration time (Section 13), and of course the adsorption curves themselves). Adsorption data generated with other mixing devices may be valid, but to insure standardized results between laboratories, these data should not be routinely accepted unless the investigator can document that these other devices yielded data comparable to those from an NBS rotary extractor or equivalent.

SECTION 9: SELECTION OF A SOIL:SOLUTION RATIO FOR IONIC SOLUTES

The term "soil to solution ratio" refers to the ratio of the mass of the adsorbent sample to the volume of liquid. For the purposes of these procedures, it shall be assumed that one milliliter of solution, regardless of its composition, weighs one gram. In order to construct an adsorption isotherm (curve), it is necessary to determine soil:solution ratios that will permit enough solute to be adsorbed to result in measurable, statistically significant differences in solution concentration. In these procedures, increasing the soil:solution ratio from a "low ratio" to "higher ratios", such as 1:1 to 1:100, means that the volume of solution increases relative to the weight of the soil material. If the soil:solution ratio was too low, i.e., too much adsorbent or too little solution, the majority of the solute initially in solution may be adsorbed, forcing the investigator to attempt to analytically measure small differences in concentration between concentrations that are low. On the other hand, if the ratio was too high, i.e., not enough adsorbent for a given volume, the changes in the initial solute concentration may be very small, forcing the investigator to measure small differences in concentration between large concentrations. Unfortunately, with inorganic and polar organic compounds, a suitable soil:solution ratio cannot be determined _a priori_. The soil:solution ratio of the ASTM 24-hour R_d procedure is 1:20 (Griffin et al., 1985). However, a single ratio cannot be used satisfactorily in all cases.

An empirical, systematic procedure to determine a suitable ratio for a given soil-water and concentration range is given in Section 17. A value of 10% to about 30% adsorption for the highest solute concentration used is a useful criterion for selecting a soil:solution ratio. This will give a discernible decrease in solute concentration that is statistically acceptable with respect to the initial concentration. Justification for this guideline is given in Section 12. An example of this type of approach is given in Table 8. Using a 1:4 soil:solution ratio, more than 90% of the cadmium initially added (200 mg/L) was adsorbed by both a Sangamon paleosol and Vandalia till sample. If the 1:4 soil:solution ratio was used to generate data at lower concentrations than the 200 mg/L used in this example, the equilibrium cadmium concentrations would be below analytical detection limits. In contrast, when a 1:500 ratio was used at the lower concentration (10 mg/L), about 60% of the cadmium initially added was adsorbed by the Sangamon sample. However, when

Table 8. Soil:solution ratio determination for the Sangamon soil and Vandalia ablation till using cadmium as the adsorbate.

Initial concentration = 200 mg/L

Soil:solution Ratio	SANGAMON		VANDALIA (ABLATION)	
	Cd adsorbed		Cd adsorbed	
	µg/g	%	µg/g	%
1:4	722	95.2	635	94.1
1:10	1631	86.1	1359	76.2
1:20	2792	73.7	2143	44.3
1:40	4246	56.0	3012	25.4
1:60	5165	45.4	3441	19.1
1:100	6250	33.0	3880	13.0
1:200	7500	19.8	4560	8.0
1:500	9250	9.8	4900	4.6
Initial concentration = 10 mg/L				
1:100	957	91.1	840	80.0
1:200	1736	82.7	1474	70.2
1:500	3178	60.5	2215	42.2
1:1000	4325	41.2	--	--

the 200 mg/L Cd solution was used, only 9.8% was adsorbed at the same soil:solution ratio. Essentially, the object is to select a soil:solution ratio that will serve as a compromise. In this case, a ratio of 1:100 was chosen to generate an adsorption isotherm because the amount of cadmium adsorbed from the high concentration range of the isotherm (200 mg/L solution) was approximately between 10% and 30%, and at the same time the amount of cadmium remaining from a low concentration (10 mg/L) solution was also within analytical detection limits.

This rationale for selecting soil:solution ratios is illustrated graphically in Figs. 16 and 17. In each figure, the amount of solute remaining in solution after 24 hours is plotted against the soil:solution ratio. The speckled area approximates the desired solute concentration after 24 hours of mixing given that about 10% to 30% of the solute is adsorbed. When the data points or lines connecting the data points fall within this speckled area or "adsorption target zone," the corresponding soil:solution ratio will usually yield satisfactory results. The adsorption behavior of seven soil materials with respect to arsenic is shown in Figure 16. In this case, a 1:10 ratio was chosen to construct adsorption isotherms with six of the seven adsorbents. Figure 17 illustrates the same concept with six samples using cadmium as the solute. A 1:10 ratio was chosen for the Tifton loamy sand, although any ratio between 1:10 to 1:4 would have probably yielded satisfactory results. A 1:20 ratio was chosen to study cadmium adsorption by the Cecil clay loam sample while a 1:100 ratio appeared to be feasible for the remaining four soil materials.

Comparison of the two figures indicates that the adsorption of arsenic was essentially a linear function of the soil:solution ratio whereas the adsorption behavior of cadmium appeared to be influenced by the soil:solution

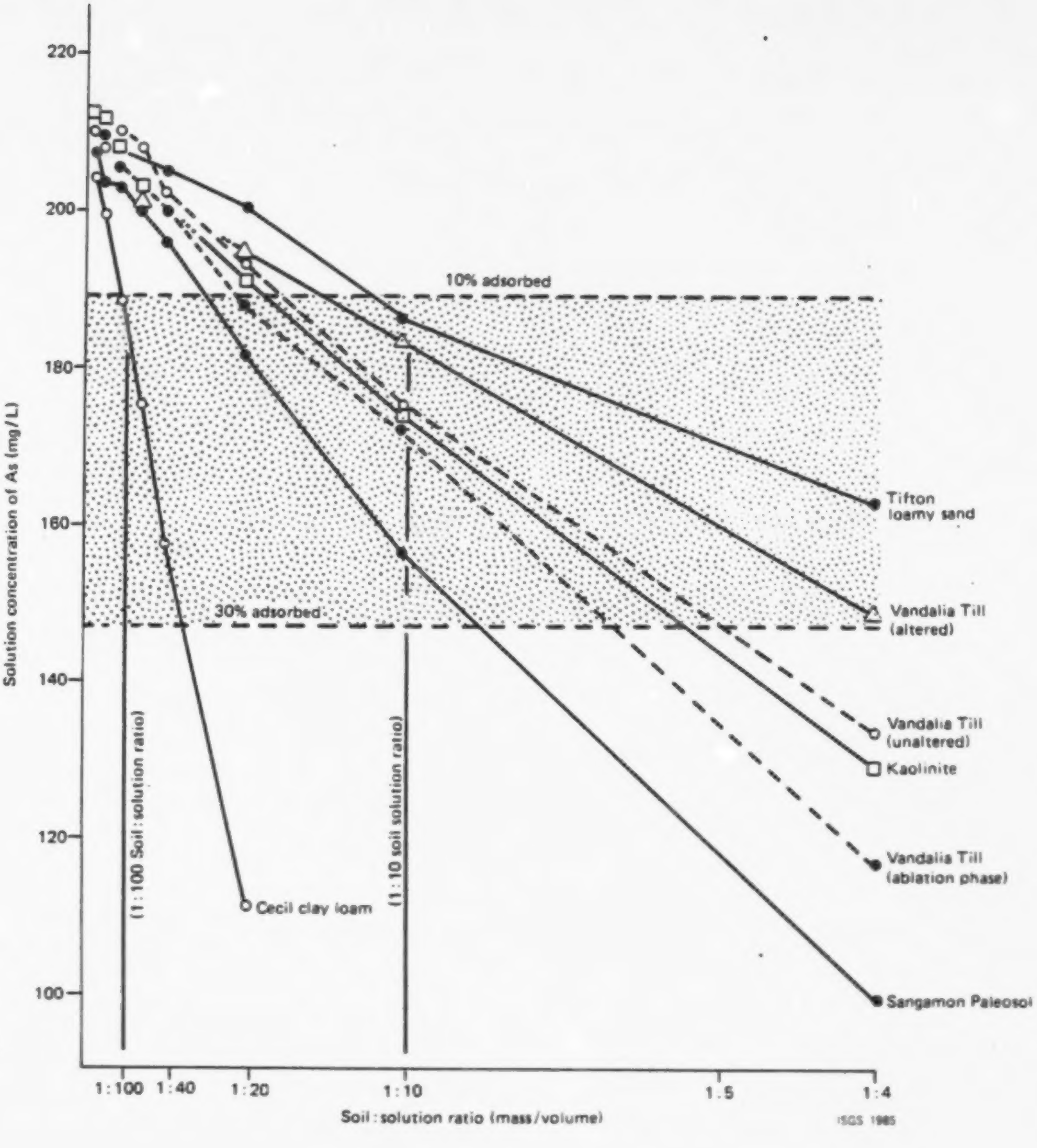

Figure 16. Distribution of arsenic concentrations after 24 hours of contact with different soil materials as a function of soil:solution ratio.

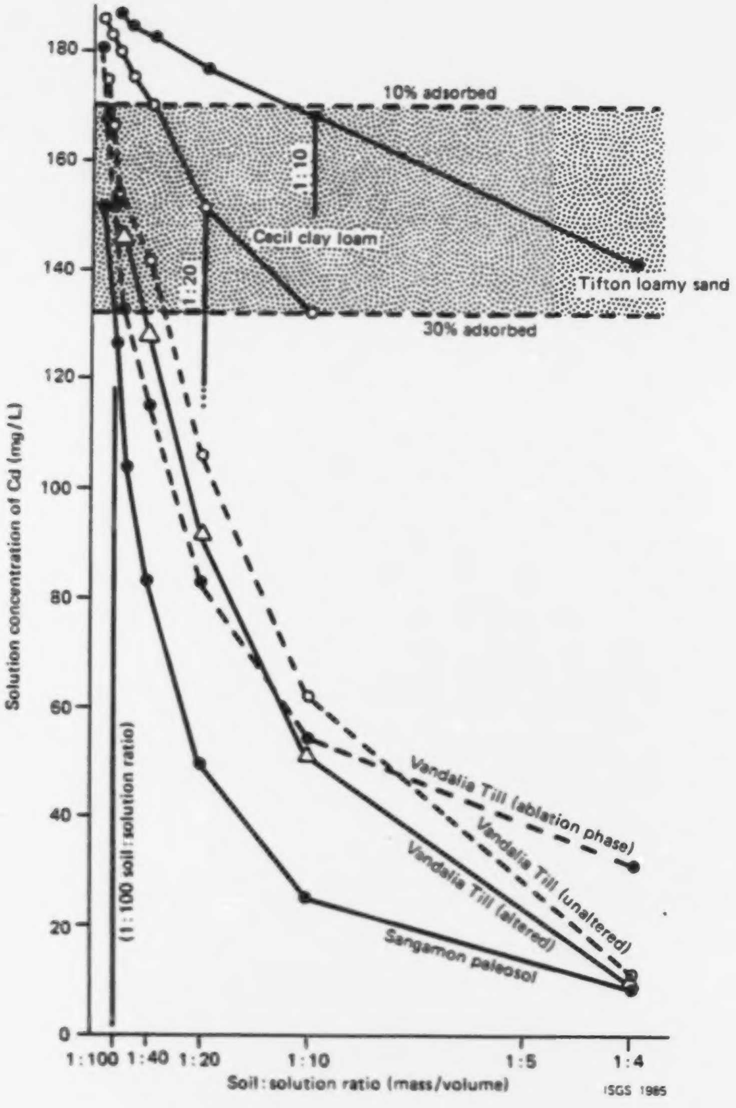

Figure 17. Distribution of cadmium concentrations after 24 hours of contact with different soil materials as a function of soil:solution ratio.

ratio; as the ratio of soil to solution decreases, progressively less cadmium was adsorbed per gram of adsorbent. The significance of this trend is discussed in the next section.

The same type of rationale may be applied to solutions containing more than one solute of interest. A laboratory extract of a metallic waste sample (see Appendix B) will help to illustrate this point. The aqueous extract of the waste contained several aqueous constituents of interest, and a suitable soil:solution ratio had to be determined for each solute. It would be ideal if one single ratio could be used for all of the solutes with each given soil but, for example, the concentration of zinc in the extract (550 mg/L) was much larger than that of barium (2.26 mg/L).

A 1:20 soil:solution ratio for the Sangamon sample (Table 9) resulted in 32.5% of the zinc being adsorbed, but using the same ratio also resulted in 96.2% of the lead in solution being adsorbed which resulted in the solution concentration of lead being very close to detection limits. When the "stock" extract was diluted to construct an adsorption isotherm, the adsorption behavior of lead could not be described using this soil:solution ratio (1:20) since most of the equilibrium concentrations of lead would be below analytical detection limits. Thus a 1:20 ratio was selected to construct a zinc adsorption isotherm, while a 1:100 ratio appeared to be useful for deriving Pb and Ba adsorption data.

Barium was adsorbed by Cecil clay loam but not to a significant extent (Table 9). Since a 1:1 ratio did not result in at least 10% adsorption, no additional experiments were done with this system. A 1:20 ratio was selected for lead adsorption by Cecil clay loam (Table 9) although any ratio between 1:20 and 1:60 would probably have been acceptable.

Table 9. Determination of soil:solution ratios for the Sangamon Paleosol and the Cecil clay loam sample using an extract of Sandoval zinc slurry.

SANGAMON SOIL			CECIL CLAY LOAM		
Solution Conc. (mg/L)	% Adsorbed	Soil:Solution Ratio	Solution Conc. (mg/L)	% Adsorbed	Soil:Solution Ratio
	Ba			Ba	
0.84	62.9	1:10			
1.15	49.1	1:20	2.09	8.7	1:1
1.80	20.3	1:60	2.19	4.4	1:2
2.00	11.5	1:100*	2.24	5.0	1:4
2.19	3.1	1:200	2.24	0.4	1:10
2.25	0.4	1:500	2.24	0.4	1:20
2.26	-	Blank	2.27	-	Blank
	Pb			Pb	
0.15	99.0	1:10	4.51	69.3	1:10
0.55	96.2	1:20	6.98	52.5	1:20*
2.64	81.2	1:60	10.8	26.5	1:60
4.70	67.8	1:100*	11.6	21.1	1:100
8.18	44.0	1:200	12.7	13.6	1:200
11.4	21.9	1:500	13.0	11.6	1:500
14.6	-	Blank	14.7	-	Blank
	Zn			Zn	
269	50.3	1:10	262	53.5	1:1
365	32.5	1:20*	365	35.3	1:2
485	10.4	1:60	444	21.3	1:4*
494	8.9	1:100	486	10.0	1:10
532	1.7	1:200	515	4.6	1:20
542	0	1:500	552	-	Blank
541	-	Blank			

* Soil:solution ratio selected for the kinetic experiments and the adsorption isotherms.

A 1:4 soil:solution was chosen to study zinc adsorption by Cecil clay loam (Table 9), although any ratio between 1:3 to about 1:8 could also be used. In some cases, there is a range of suitable soil:solution ratios for a given soil, but even this range of values must be found experimentally. However, as discussed in Section 11, there are guidelines for selecting ratios within the acceptable range. Thus three different soil:solution ratios (1:4, 1:20, 1:100) were used to construct barium, lead, and zinc adsorption isotherms with the two soil samples (results shown in Appendix B).

SECTION 10: SELECTION OF A SOIL:SOLUTION RATIO FOR NONIONIC SOLUTES

While finding a suitable soil:solution ratio for ionic and polar solutes requires laboratory work, there is a simple calculation that can be used to estimate a suitable ratio for nonionic solutes, particularly hydrophobic organic species. This estimation technique requires a value for the organic carbon content of the adsorbent and for the organic carbon partition coefficient (K_{oc}) of the solute (McCall, 1981).

A derivation of this estimation technique begins with:

$$\text{let} \qquad K_d = \frac{\mu g_s \text{ solute/g soil}}{\mu g_w \text{ solute/g solution}} = \frac{\mu g_s/g}{\mu g_w/g} \qquad [4]$$

where K_d is equivalent to the Freundlich constant K_f (refer to Section 14) in the special case where the isotherm in linear (i.e., $^1/n$ is unity), and

$\mu g_s/g$ is the mass of solute adsorbed per gram of the adsorbent, and

$\mu g_w/g$ is the mass of solute per gram of solution.

Also, let R = g adsorbent/g aqueous solution. If we assume that the weight of the solution is approximately equal to its volume (i.e., 1 mL ≈ 1 g), then R is the soil:solution ratio. Eq. [4] becomes

$$K_d = \frac{\mu g_s}{\mu g_w} \left(\frac{1}{R}\right) \qquad [5]$$

Since $\mu g_s + \mu g_w$ should equal the total mass of solute initially added (μg^0) assuming that losses due to volatilization or microbial degradation are negligible, then

$$K_d = \frac{\mu g_s}{(\mu g^0 - \mu g_s)\, R} \qquad [6]$$

or

$$R = \frac{\mu g_s}{(\mu g^0 - \mu g_s)\, K_d} \qquad [7]$$

Thus, it is possible to select an appropriate soil:solution ratio (R) based on an estimate of the K_d value of the specific solute-adsorbent system. An estimation of K_d can be calculated if the organic carbon content (OC) of the adsorbent and the K_{oc} of the solute are known by

$$K_d = K_{oc}\ (\%OC)/100 \qquad [8]$$

The organic carbon partition coefficient (K_{oc}) of many hydrophobic and other organic solutes have been compiled and are given elsewhere (Kenaga, 1980; Kenaga and Goring, 1980; Banerjee et al., 1980; Hassett et al., 1983; Griffin and Roy, 1985; and Roy and Griffin, 1985). Many of the K_{oc} values that have been reported were based on empirical equations that relate the solubility (S) of the solute in water to its organic carbon partition coefficient (K_{oc}), such as the expression given by Hassett et al. (1983), viz.,

$$\log K_{oc} = 3.95 - 0.62 \log S\ (mg/L) \qquad [9]$$

A similar linear relationship has been observed relating the octanol-water partition coefficient to its organic carbon partition coefficient, such as the version given in Hassett et al. (1983), viz.,

$$\log K_{oc} = 0.088 + \log K_{ow} \qquad [10]$$

A compilation of octanol-water partition coefficients was published by Leo et al. (1971). The historical evolution of these concepts was discussed by Griffin and Roy (1985).

To illustrate the application of this estimation technique, the adsorption behavior of a ternary-solute mixture containing dichloroethane, tetrachloroethylene, and o-xylene by a Catlin silt loam sample was studied. In order to construct adsorption isotherms, suitable soil:solution ratios for each solute had to be determined. The organic carbon content of this soil sample was 4.04%. An estimate of a K_d value for each solute was based on its water solubility using eq. [9].

The solubility of dichloroethane and tetrachloroethylene is 8450 mg/L and 200 mg/L respectively at 25°C (Chiou et al., 1979), and the solubility of o-xylene is approximately 175 mg/L at 25°C (McAuliffe, 1966). Using eqs. [8] and [9], the calculated K_d values of dichloroethane, tetrachloroethylene, and o-xylene were approximately 1.3, 13.4, and 14.7, respectively. Recall from Section 9, a soil:solution ratio corresponding to about 10 to 30% adsorption is a useful criterion for selection a suitable ratio. Thus, assuming that 20% adsorption will fall into the "target zone" for each of the organic solutes, $\mu g_s/\mu g^o$ is set equal to 20. Then the soil:solution ratio for each solute may be calculated by arbitrarily setting μg^o equal to 100. For example,

tetrachloroethylene:

$$R = \frac{20}{(100-20)\ 13.4} = \frac{1}{53.6}$$

o-xylene:

$$R = \frac{20}{(100-20)\ 14.7} = \frac{1}{58.8}$$

There is no reason to work with such awkward numbers for the actual measurements. These soil: solution ratios could be simplified to 1:50 and 1:60. As discussed in Section 9, it would be fortuitous when a single soil:solution ratio could be used to generate an adsorption isotherm for every solute of interest in a multicomponent mixture. In this example, a 1:50 ratio was selected for the mixture to generate adsorption isotherms for each solute as shown in Figs. 18 and 19; a single ratio was suitable in this case. This also illustrates that there may be a range of suitable ratios for some organic solutes, but Section 11 should be consulted for guidelines for selecting suitable ratios.

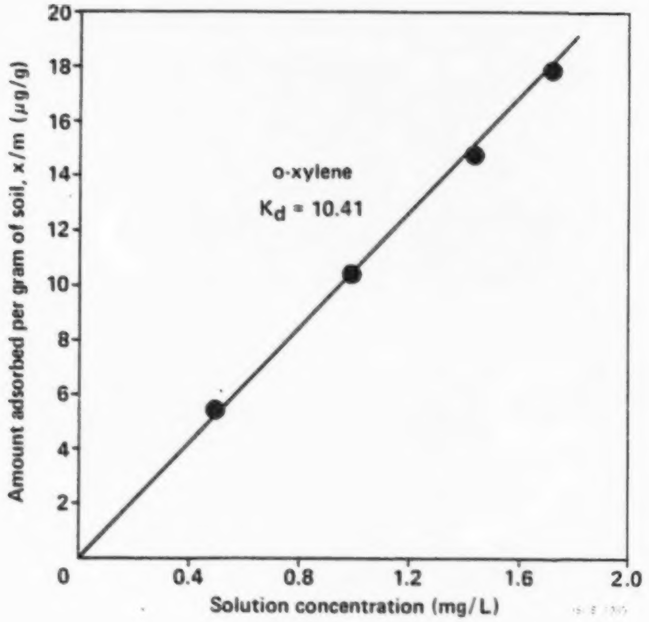

Figure 18. Adsorption isotherm of o-xylene by Catlin at 23°C, and at pH 6.1.

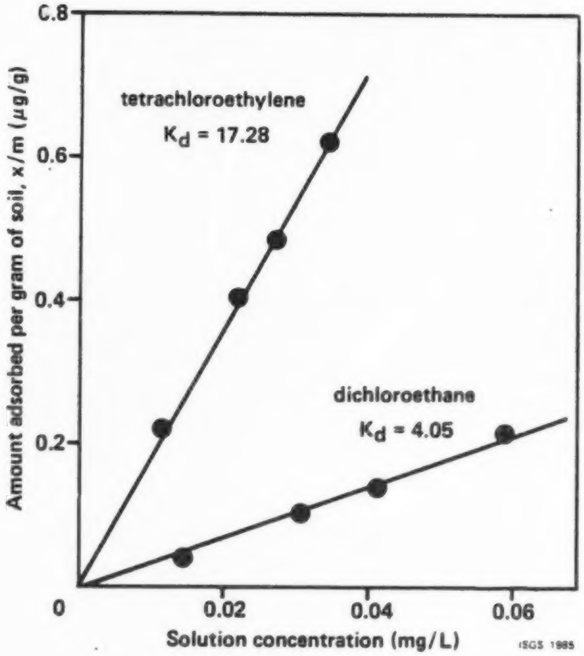

Figure 19. Adsorption isotherms of dichloroethane and tetrachloroethylene by Catlin at 23°C, and at pH 6.1.

This estimation technique can be generalized and shown as a relationship between the linear Freundlich constant (K_d) and the soil:solution ratio (R), as a function of different amounts of adsorption on a percentage basis (Figs. 20 and 21). McCall et al. (1981) demonstrated that eq. [5] could be rearranged as:

$$\frac{1}{R} = ((\mu g^o/\mu g_s) - 1)\ K_d \qquad [11]$$

which was used to generate Figs. 20 and 21. These figures should serve as convenient guides for selecting soil:solution ratios. For example, the solubility of carbon tetrachloride in water is 800 mg/L at 25°C. The K_{oc} value, estimated using eq. [9], was 140. Using a Catlin silt loam sample with an organic carbon content of 4.04%, a K_d value was calculated as

$$K_d = \frac{140\ (4.04)}{100} = 6 \qquad [12]$$

Reading from Figure 20, a soil:solution ratio of about 1:10 should yield approximately 30% adsorption.

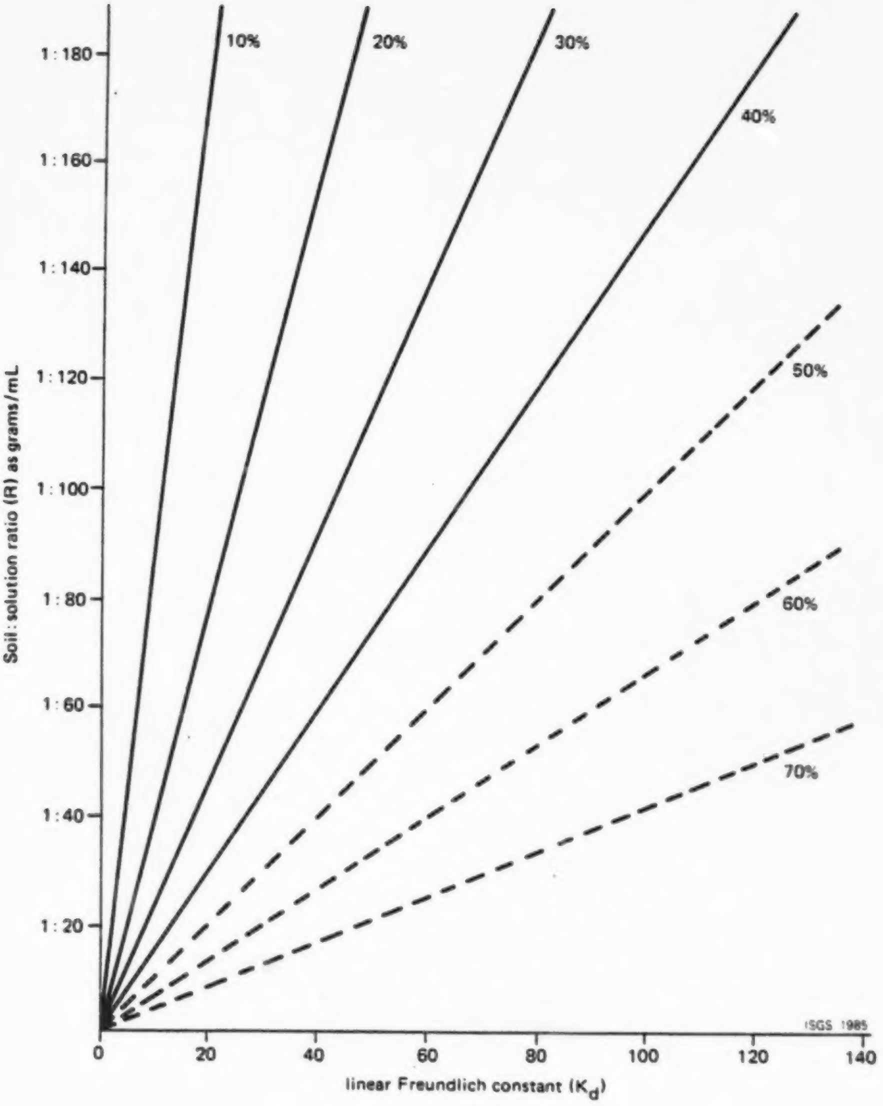

Figure 20. Relationship between the linear Freundlich constant (K_d) and soil: solution ratio, as a function of percent adsorption (lower range).

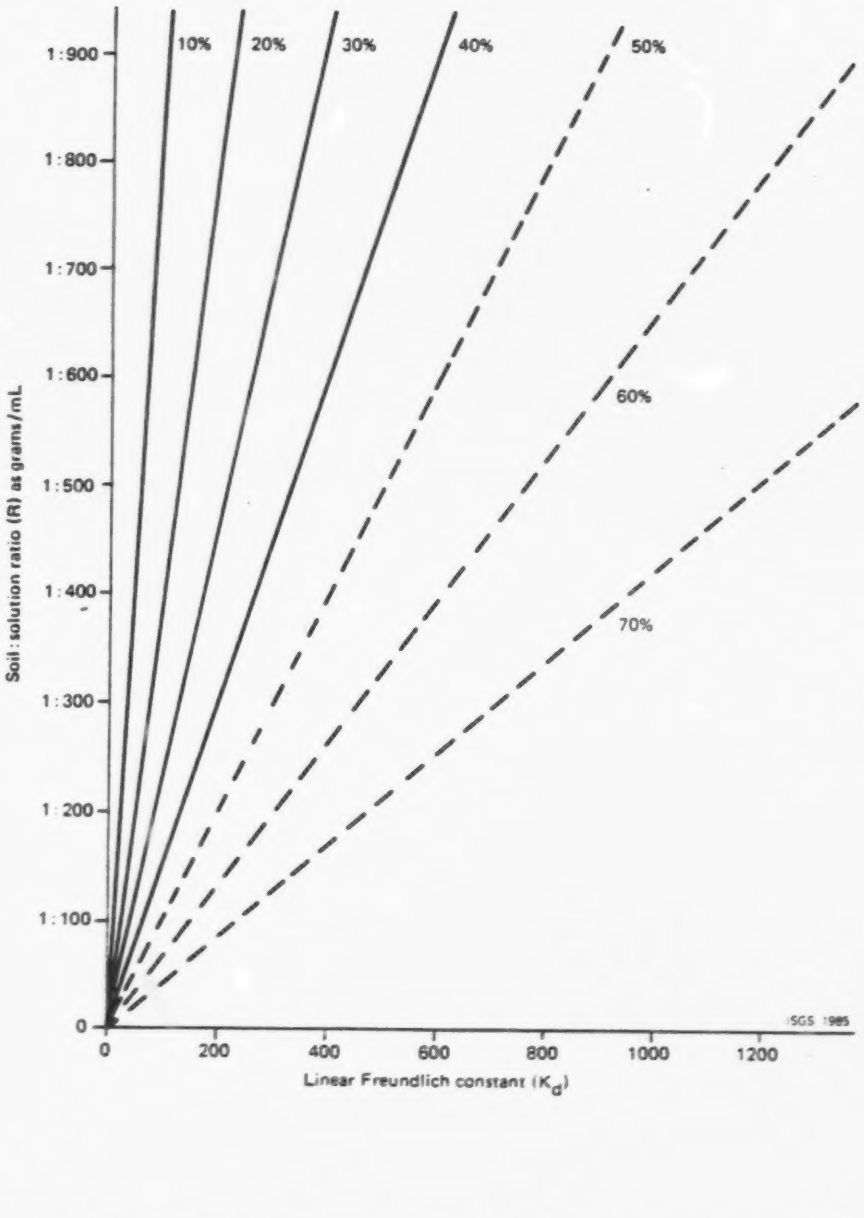

Figure 21. Relationship between the linear Freundlich constant (K_d) and soil: solution ratio, as a function of percent adsorption (upper range).

SECTION 11: EFFECTS OF THE SOIL:SOLUTION RATIO

The soil:solution ratio may be one of the most important experimental variables to consider when constructing an adsorption isotherm and evaluating the adsorption data, particularly when comparing results from different investigators using different ratios. In Figure 18, increasing the amount of adsorbent while holding the volume of solution constant had the effect of increasing the mass as well as surface area on which the arsenate ions could be adsorbed. Hence, intuition suggests that as the amount of adsorbent is increased, the amount of arsenic left in solution after exposure should decrease in an essentially uniform manner as shown in Fig. 16.

Figure 17 demonstrated a non-linear response; the amount of cadmium left in solution after 24 hours appeared to be approaching a constant value as the amount of adsorbent was increased (i.e., the soil: solution ratio was decreased). There is no single explanation for all systems for this non-linear response or what White (1966) called the "soil:solution ratio effect." This phenomenon does not negate the selection of a soil:solution ratio, but the consequences of that selection must be considered.

The soil:solution ratio effect and the adsorption of phosphate has probably received the most attention, although there are conflicting reports concerning its effects (Barrow and Shaw, 1979). Phosphate adsorption was increased by the use of high soil:solution ratios in the studies of Fordham (1963), Barrow et al. (1965), and White (1966). Hope and Syers (1976) found that high ratios resulted in lower phosphate adsorption. An early paper by Kurtz et al. (1946) found no soil:solution ratio effect (i.e., a linear response) when studying phosphate adsorption by Illinois soils.

White (1966) attempted to reconcile his results by arguing that the system was not at equilibrium. However, this line of reasoning contradicted his rationale for selecting an equilibration time. Larsen and Widdowson (1964) had concluded two years earlier that the soil:solution ratio effect was due to an increase in microbial activity as the mass of the soil was increased.

Hope and Syers (1976) argued that different soil:solution ratios affected only the rate at which phosphate was removed from solution. They found that the change in solution phosphate concentration when mixed with their soils was proportional to the reciprocal of time. Thus, when the reciprocal-time scale was extrapolated to zero, i.e., infinite time, the effects of different soil:solution ratios disappeared; the isotherms merged into a single point. They concluded from this analysis that about 2 to 3 months of equilibration would be necessary in order for soil:solution effects to essentially disappear and thus the adsorption data would be essentially independent of the soil:solution ratio, approaching the expected linear response.

This hypothesis was challenged by Barrow and Shaw (1979) who found that the reciprocal-time analysis used by Hope and Syers (1976) did not explain the soil:solution ratio effects observed in their study. Barrow and Shaw (1979) concluded that such effects were related to particle breakdown during shaking. As more soil was used (i.e., as the ratio decreased), more particles broke down, exposing "new" adsorption sites available to phosphate. However, this concept does not explain the results shown in Figure 17.

While the mechanisms proposed above may be operative in some systems, the soil:solution ratio effect has often been attributed to the competitive interactions between a given solute and species that are concommitantly desorbed or exchanged during the partitioning of solutes and adsorbates. As the amount of adsorbent is increased, there is a larger source of these potentially competing constitutents. The net effect is that the magnitude of adsorption (given equal initial concentrations) decreases. For example, Griffin and Au (1977) found that the adsorption of lead progressively decreased as the sample size of a calcium-saturated montmorillonite was increased. As the amount of adsorbent was increased, the amount of calcium that was desorbed or exchanged from the clay also increased and competed with lead for adsorption sites.

A similar phenomenon was observed in this study in which the adsorption characteristics of a Sangamon paleosol were investigated using $CdCl_2$. There was a strong soil:solution ratio effect on cadmium adsorption (Fig. 22). The curvilinear distribution of data points was derived by using a 1:100 soil:solution ratio. However, when different soil:solution ratios were used, the resulting data did not follow the same pattern but fell on a nearly straight line that intersected the adsorption curve obtained where 1:100 ratios were used.

It was suspected that Ca^{2+} and Mg^{2+} were exchanging with cadmium and thus reducing cadmium adsorption. Hence the greater the amount of sample, the larger the amount of Ca^{2+} and Mg^{2+} capable of competing with cadmium. At any given equilibrium concentration of cadmium, higher soil:solution ratios (i.e., less adsorbent per volume of liquid) were associated with increased cadmium adsorption.

The Sangamon sample contained about 50% expandable clays and 40% illite (Appendix A). Work by Bittel and Miller (1974) indicated that selectivity coefficients for Ca^{2+} and Cd^{2+} exchange reactions with montmorillonite, illite and kaolinite were between 0.8 and 1.3 (on a concentration basis), suggesting

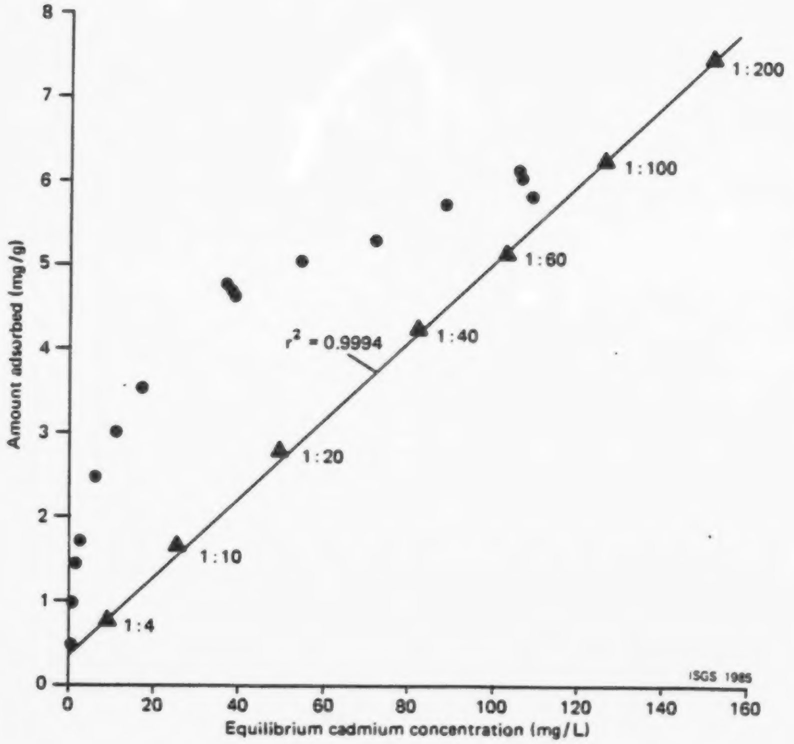

Figure 22. Effect of soil:solution ratio on cadmium adsorption by a Sangamon paleosol sample at pH 6.1, and at 22°C. The solid dots were derived by using a 1:100 ratio (Roy et al., 1984).

that these clay minerals have no strong affinity for one cation versus the other over a pH-range of approximately pH 5 to pH 7 (c f. Bolt and Bruggenwert, 1978). Calcium will readily exchange with cadmium and vice versa. If the adsorption data are plotted as cadmium adsorbed relative to $Cd^{2+}/(Ca^{2+} + Mg^{2+})$ on a molar basis (Fig. 23), the different soil:solution ratios coalesced into one adsorption curve.

The soil:solution ratio can also influence the chemical composition of the system which in turn can directly or indirectly affect adsorption data. It is a well-established practice to generate aqueous extracts of soil samples to make qualitative assessments for soil management. Reitemeir (1945) reviewed the literature on the effects of dilution on ionic concentration in soil solutions and attempted to generalize the results:

Nonsaline soils:

1. Solution potassium increased with dilution
2. Calcium and magnesium in solution frequently increases with dilution while the ratio of Ca:Mg changes
3. Phosphorus usually increases proportionally to dilution

Alkali, calcareous, and gypsiferous soils:

In virtually all cases, dilution results in increased amounts of Ca, Mg, Na, K, SO_4, P, and Si

Thus the ionic concentrations in soil solutions and soil extracts are not inversely proportioned to the amount of water present.

The pH of the soil-liquid suspension will also be affected by the soil:solution ratio. The relationship between pH and adsorption is discussed in Section 5. The pH of a soil suspension in a batch adsorption procedure will be controlled by three factors:

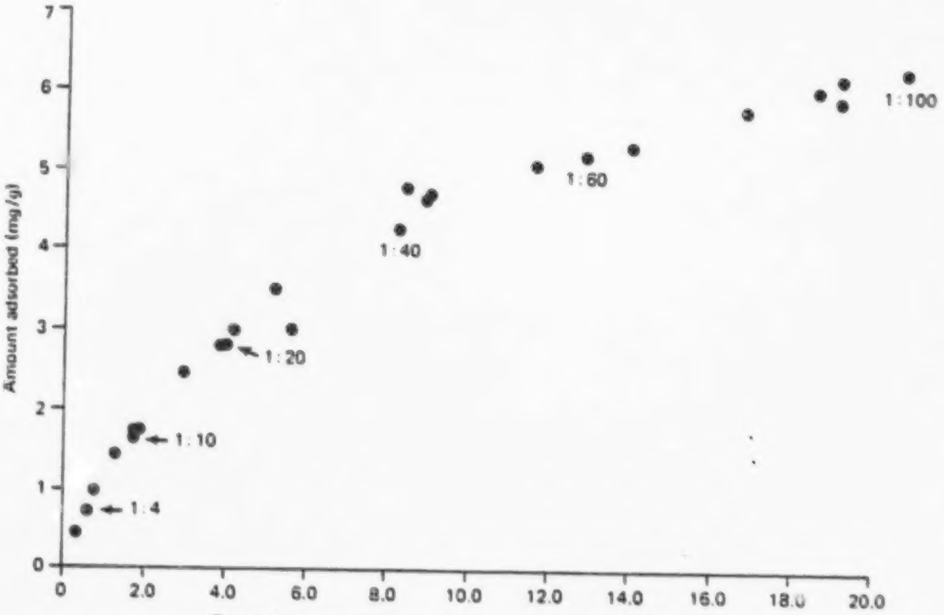

Figure 23. Cadmium adsorption by a Sangamon paleosol sample. The adsorption curve shown is a transformation of Figure 22, taking competitive interactions of Ca^{2+} and Mg^{2+} into account (Roy et al., 1984).

1. the "natural" pH of the adsorbent and its buffering capacity to maintain that pH
2. the pH and composition of the liquid phase
3. adsorption reactions that directly or indirectly change the H_3O^+ and/or OH^- concentration in solution.

The first two factors are illustrated by Figures 24 and 25. The equilibrium pH of solutions mixed with eight soil materials are plotted against the soil:solution ratio. In Figure 24, the soil materials were exposed to an sodium arsenate solution containing 200 mg/L As with an initial pH of 4.65. Consequently, at progressively higher ratios (i.e., more dilute systems), the pH of the solutions became progressively closer to that of the arsenate solution. Thus, at ratios of approximately 1:20 or higher, the pH of the arsenate solution dominated the pH of the suspensions. At lower soil:solution ratios, the equilibrium pH of each solution became more like that of the soil, the relative strength of this tendency depending on the pH buffering capacity of the soil.

In the second example (Fig. 25) the soil materials were exposed to a cadmium chloride soltuion containing 200 mg/L Cd with an initial pH of 5.45. A 1:20 ratio for a kaolinite clay sample (Fig. 25) was associated with a solution pH of 7.05, while a 1:4 ratio resulted in a solution pH of 7.45, an increase of 0.4 pH units. Thus an isotherm generated with a 1:4 ratio may yield lower amounts of cadmium adsorption than one using a 1:20 ratio simply because the pH of the former tended to be more basic for reasons discussed in Section 5.

A similar type of relationship may be observed with complex, multicomponent extracts or leachates. The equilibrium pH of the zinc slurry extract (Appendix B) was plotted against soil:solution ratio using two soils

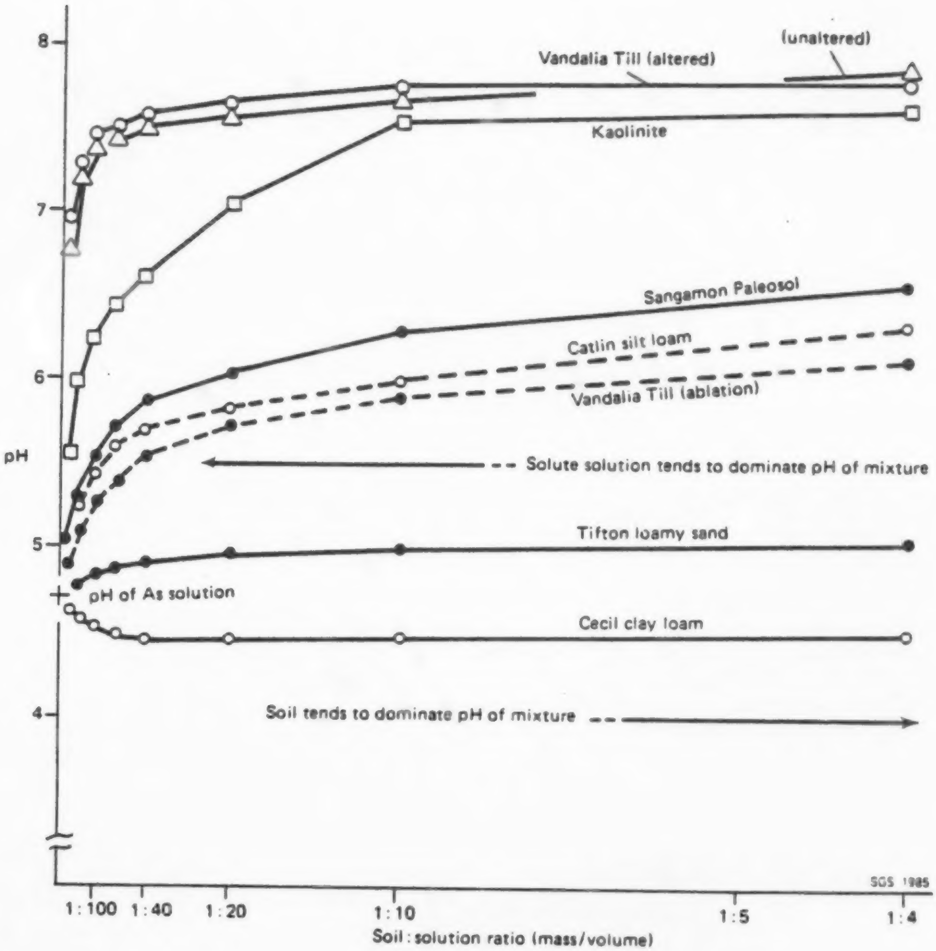

Figure 24. Distribution of pH values of arsenate solutions (containing the same initial arsenate concentration) after 24 hours of contact with different soil materials as a function of soil:solution ratio.

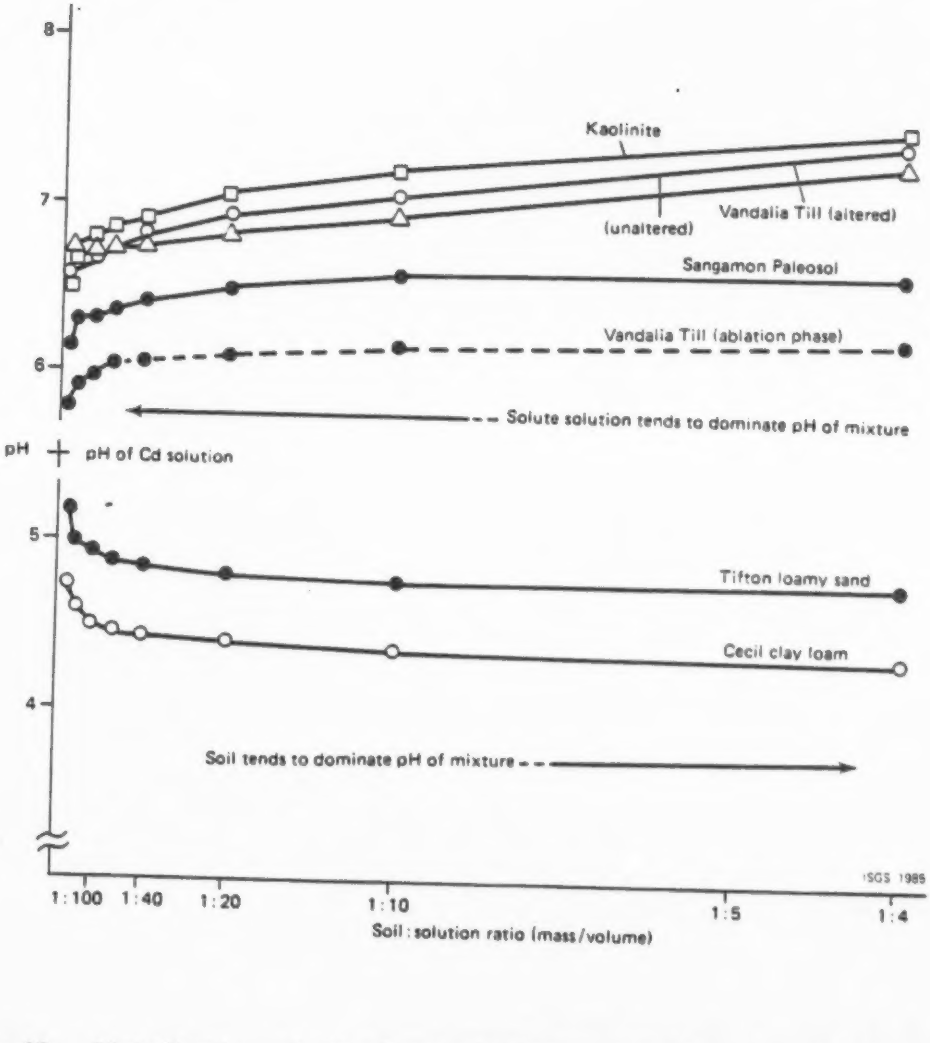

Figure 25. Distribution of pH values of cadmium solutions (containing the same initial cadmium concentration) after 24 hours of contact with different soil materials, as a function of soil:solution ratio.

(Fig. 26). In both cases, lower soil:solution ratios tended to be associated with pHs lower than that of the extract. However, the pH tended to be constant when a 1:10 or smaller ratio was used.

The soil:solution ratio will often influence the ionic strength of the solution. This is to be expected since the ionic strength of any solution would be controlled by the concentration and charge of both the solute(s) under study, desorbed or exchanged ions, and/or other aqueous ions derived from the dissolution of soluble minerals that naturally occur in the adsorbent. The ionic strength of the solutions in contact with the Tifton loamy sand and the Cecil clay loam tended to decrease as the soil:solution ratio decreased (Fig. 27). This trend was attributed to two factors: 1) as the ratio decreased, more arsenic or cadmium was removed from solution which lowered the ionic strength, and 2) these two soils contained a low content of water soluble compounds that contributed to the ionic strength upon dissolution. The other three soil materials (Fig. 27) were slightly calcareous by comparison and consequently lower ratios resulted in an increase in ionic strength due to dissolution of slightly soluble minerals. Discernible decreases caused by the removal of cadmium were masked by the dissolution of carbonates. Whether these changes or differences in ionic strength will have a major impact on the adsorption data is difficult to generalize (see Section 6). No routine adsorption procedure designed to be relatively simple can address this problem completely. Defining the relationship between ionic strength, soil:solution ratio, and adsorption for any soil-solute(s) system may be a large project in its own right.

The adsorption of organic solutes may also be influenced by the soil:solution ratio used in batch procedures. Grover and Hance (1970) found that the Freundlich constant (K_f) decreased significantly by a factor of 2.6

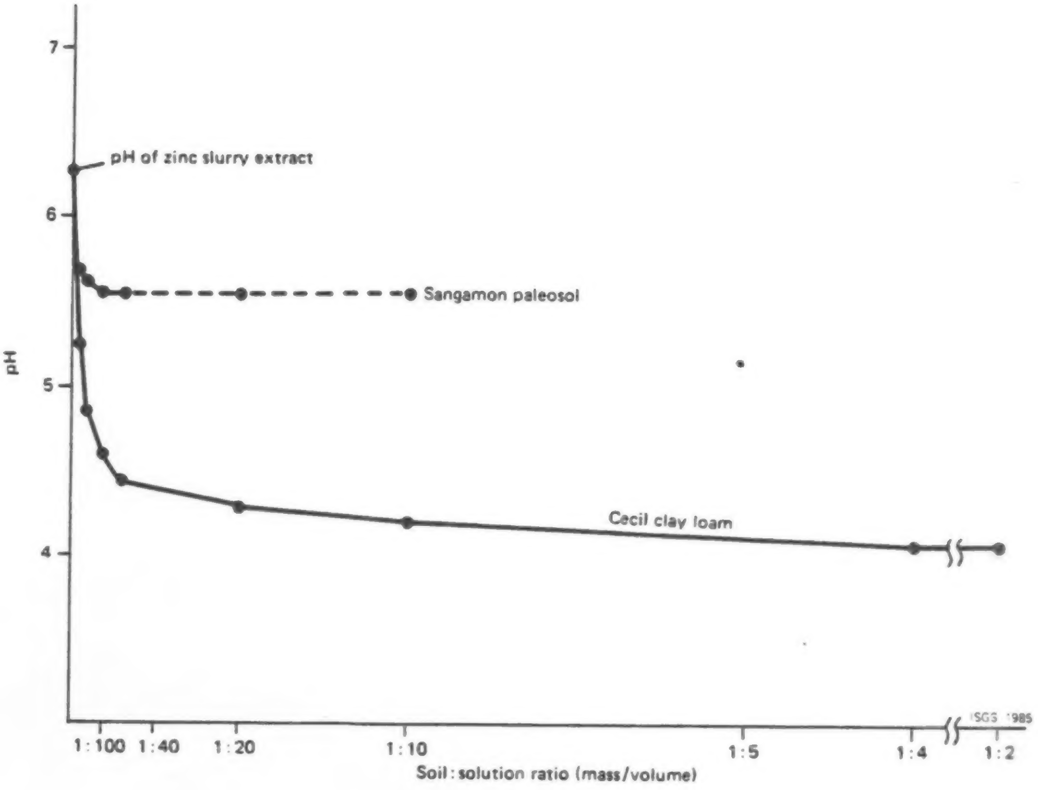

Figure 26. Distribution of pH values of solutions of the zinc slurry extract after 24 hours of contact with two soil samples as a function of soil:solution ratio.

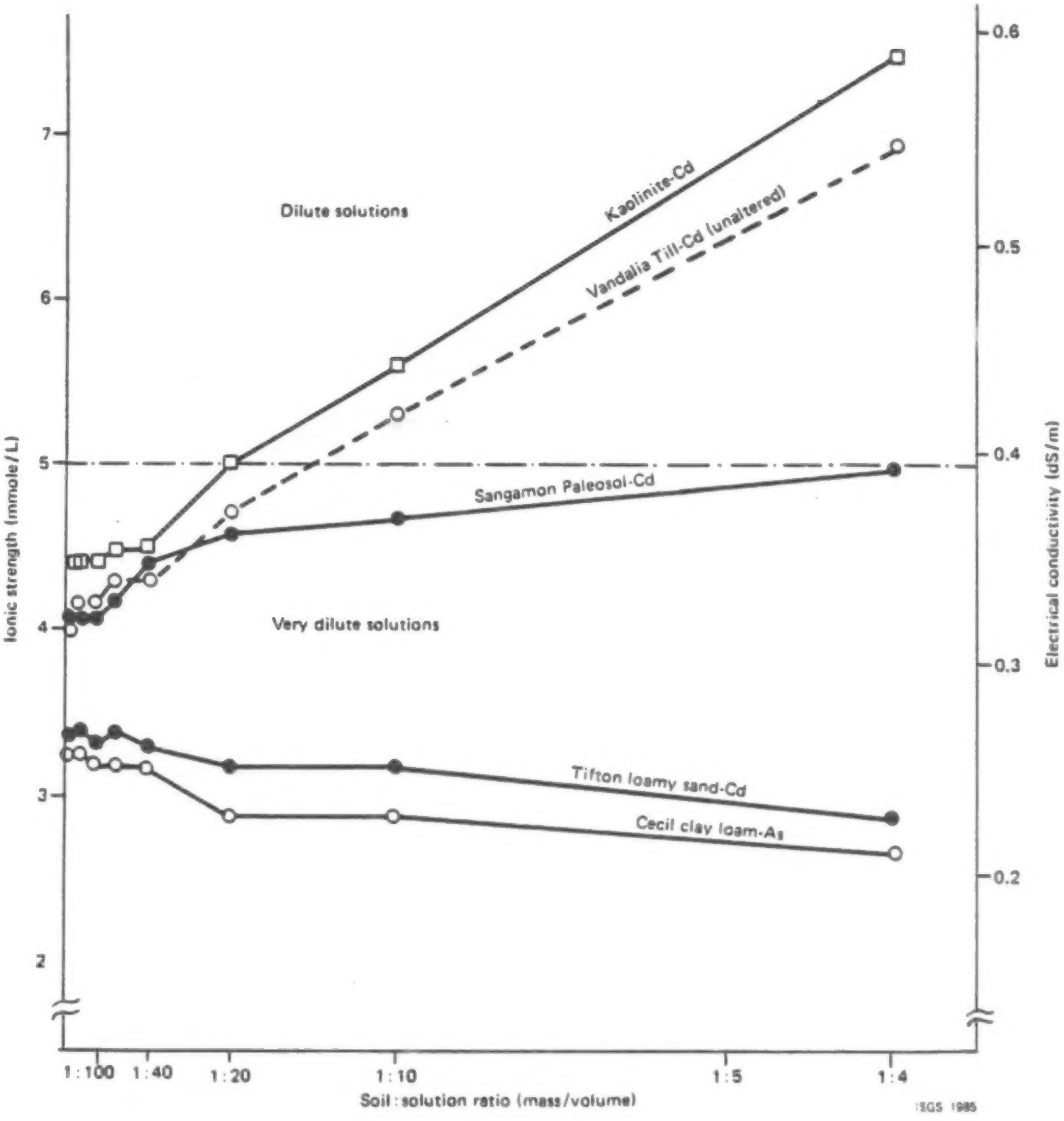

Figure 27. Distribution of the ionic strength of solution containing either arsenate or cadmium after 24 hours of contact as a function of soil:solution ratio.

as the soil:solution ratio was decreased from 1:10 to 1:0.25 in a study concerned with linuron and atrazine adsorption. They suggested that a likely cause for the differences in the extent of adsorption was related to the aggregate size of the soil. In a comparison of the relative soil particle sizes at three soil:solution ratios they placed 10 g of soil which had been passed through a No. 10 mesh sieve into flasks. The flasks were shaken with 2.5, 10, and 100 mL of a 0.1 M $CaCl_2$ solution, mixed by shaking gently end-over-end for 30 seconds, and then allowed to stand. They found that the dispersion of soil aggregates was greater at the 1:10 soil:solution ratio than at the 1:0.25 ratio; the 1:1 ratio was intermediate. A similar sedimentation behavior was also observed in the absence of 0.1 M $CaCl_2$. Thus they concluded the extent of adsorption of linuron and atrazine is related to the aggregate size of the soil.

Voice et al. (1983) reported that the solids concentration seemed to significantly affect the adsorption of several hydrophobic pollutants by Lake Michigan sediments. They concluded that the soil:solution effect in this case appeared to result from the presence of soluble microparticles derived from the soil which also tended to retain the solutes (see also Voice and Weber, 1985). They concluded that soil:solution effects reported in the literature may have been due to incomplete phase separation during centrifugation or to accumulative relative errors in measuring concentrations.

Similar conclusions were also reached by Gschwend and Wu (1985). If precautions are taken to eliminate or account for nonsettling (or nonfilterable) microparticles or organic macromolecules, which remain in the aqueous phase during batch adsorption procedures, the observed partition coefficients (K_f or K_{oc}) were found to remain constant over a wide range of soil:solution ratios. Figure 28 showed that a succession of prewashing treatments of

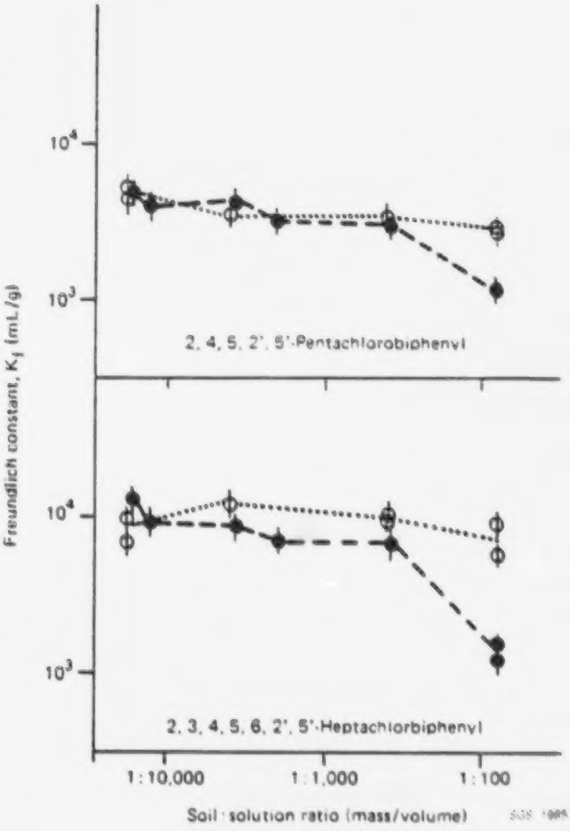

Figure 28. Freundlich constant (K_f) for two PCB isomers vs. sediment concentration with (open symbols) and without (closed symbols) prewashing to remove nonsettling particles. (adapted from Gschwend and Wu, 1985)

sediments greatly reduced the effects of the nonsettling particles (NSP). When prewashed sediments were used for batch equilibration experiments, the observed K_f remained virtually constant over the range of soil:solution ratios tested. This relationship was most dramatically shown for the partitioning of the hydrophobic compound, 2,3,4,5,6,2',5'-heptachlorobiphenyl, and the difference in K_f with and without prewashing clearly reflected the great sensitivity of very strongly adsorbed compounds to small NSP concentrations in the aqueous phase.

Voice and Weber (1985) concluded that while soluble microparticles could play the major role in the soil:solution ratio effect with regard to the adsorption of organic solutes, they felt that it could not account for all of the data given in the literature. They proposed a hypothesis where the soil:solution effect was the result of a "complexation phenomenon" whereby organic matter in the solution phase forms complexes with the solute. The solute can exist as a complexed and uncomplexed state in solution, and possibly in other solution states.

In other organic solute-adsorbent systems, the adsorption behavior of the solute was not influenced by the soil:solution ratio. Bowman and Sans (1985) reported that the adsorbent concentration (soil:solution ratio) did not appear to significantly affect the partitioning of several pesticides in sediment-water systems over a fairly wide range of values.

The adsorption of Aroclor 1242 was not influenced by the soil:solution ratio (Fig. 29). The Freundich constant was essentially constant over a wide range of soil:solution ratios. When different soil:solution ratios were used in the construction of adsorption isotherms, the resulting data tended to plot on the same line (Figures 30 and 31) and the slopes of the adsorption isotherms were nearly unity. In some cases, a curvilinear distribution of

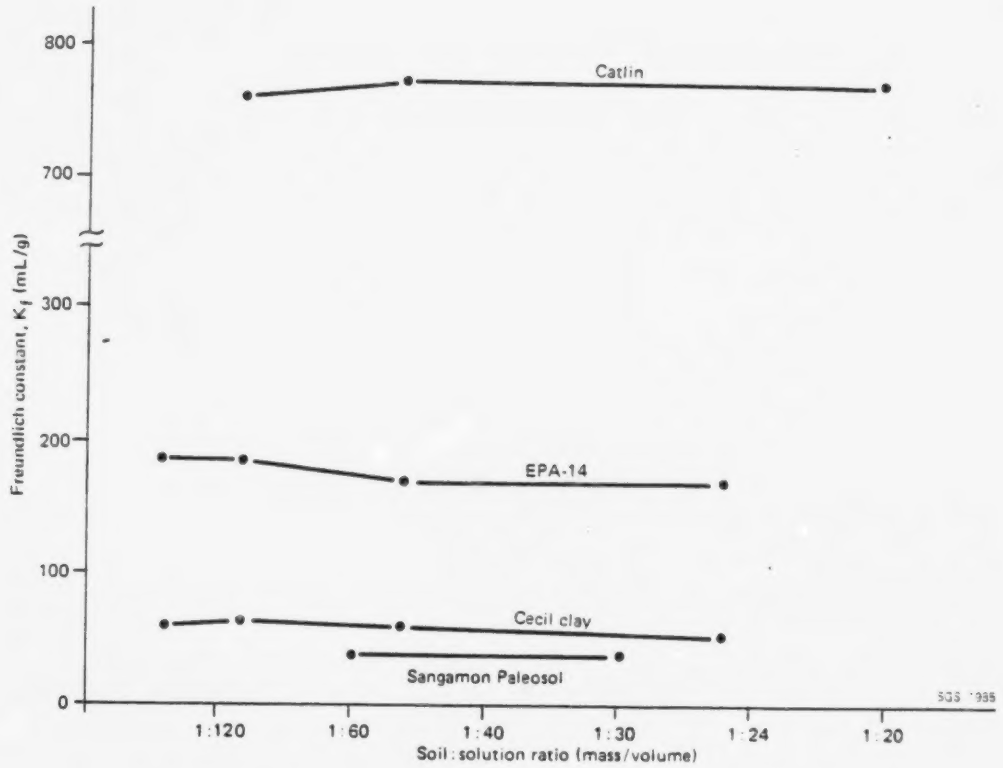

Figure 29. The Freundlich constant (K_f) for the adsorption of Aroclor 1242 by four different soils at 23°C as a function of soil:solution ratio.

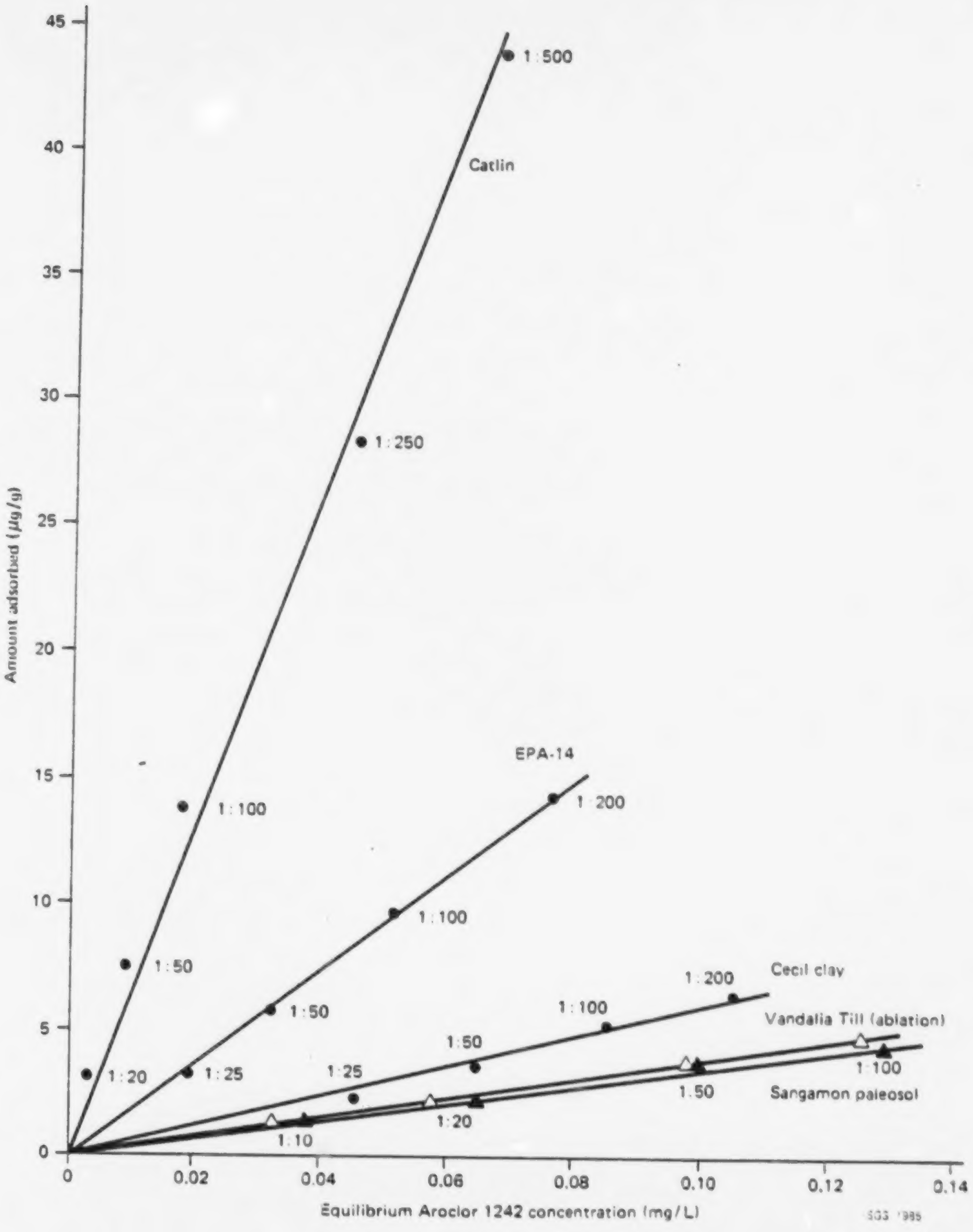

Figure 30. Aroclor 1242 adsorption isotherms by five soils at 23°C using various soil:solution ratios.

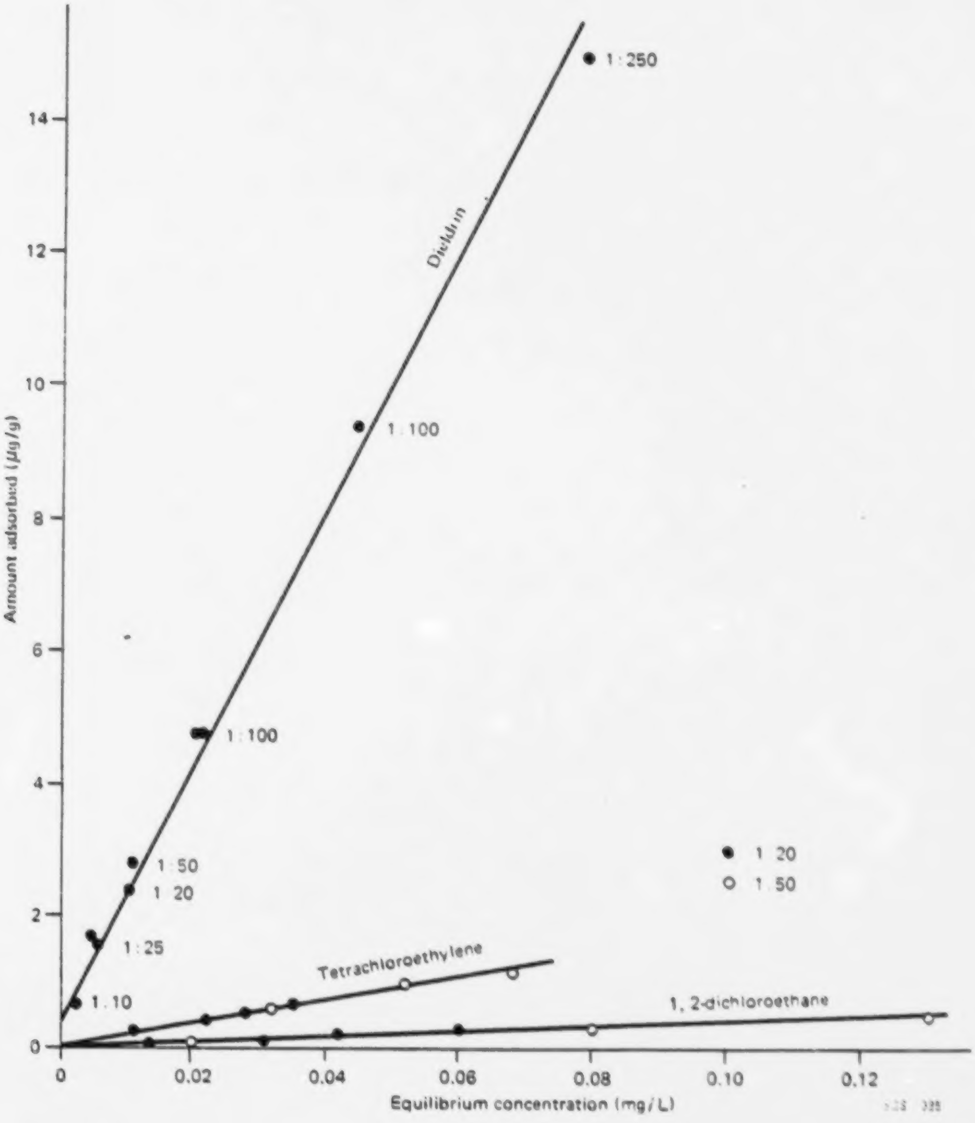

Figure 31. Adsorption of dieldrin, tetrachloroethylene, and 1,2-dichloroethane by Catlin at 23°C using various soil:solution ratios.

data points was derived by using different soil:solution ratios with some adsorbents (Figure 32). However, the application of different soil:solution ratios still yielded a single, consistent relationship between the amount of Aroclor 1242 in solution and the amount retained by the tills at equilibrium (Figure 32).

In summary, the selection of a soil:solution ratio may or may not have a profound effect on adsorption data. The soil:solution ratio may influence the pH, ionic strength, and chemical composition of the suspension which in turn may influence adsorption data. In some cases, such as competitive interactions, the soil:solution ratio effect can be rationalized, but in other systems, the ratio effect presents problems, particularly for procedures intended for the routine collection of batch adsorption data. Voice et al. (1983) commented that it is possible that some combination of techniques or new methodologies will evolve (to handle the ratio effect), but no simple solutions are readily apparent.

- In Section 17, specific soil:solution ratios are suggested for the construction of adsorption isotherms. It is strongly recommended that these ratios and only these ratios be used to ensure that different users will use the same ratios regardless of the solute-adsorbent system under study. Thus these ratios (Section 17.8.3) could be regarded as "standard soil:solution ratios." For example, if it appears that a 1:8 ratio is satisfactory for the generation of adsorption data, the investigator should attempt to use a 1:10 ratio, i.e., one of the "standard ratios". As shown in Section 9, for many systems, there will be a range of suitable ratios. The user should not arbitrarily select any ratio within this range, but should select the closest "standard" ratio. These "standard" ratios range from 1:4 to 1:10,000 and should accommodate most situations. Adherence to this recommendation will

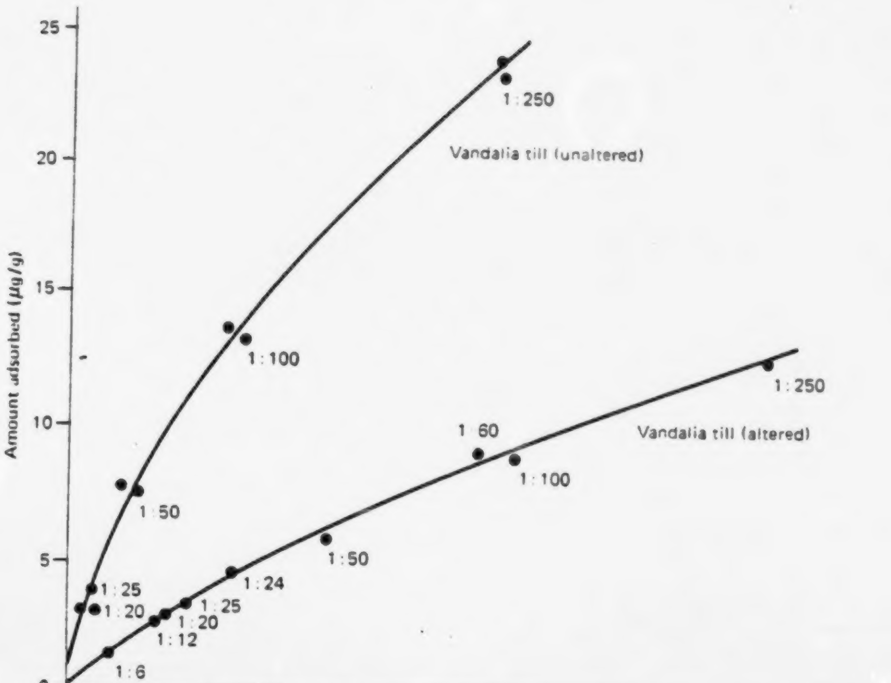

Figure 32. Adsorption of Aroclor 1242 by altered Vandalia till and unaltered Vandalia till at 23°C using various soil:solution ratios.

enable the direct comparisions of adsorption data generated by different investigators. Adsorption data based on ad hoc ratios may provide a basis for limited comparisons, but there will always be some doubt that the results are comparable unless it can be clearly shown that a particular solute-adsorbent system is not subject to soil:solution ratio effects.

SECTION 12: CONSTANT AND VARIABLE SOIL:SOLUTION RATIOS

Basically, there are two experimental techniques in generating batch adsorption data:

1. Mixing a batch of solutions, arranged in progressively decreasing solution concentrations, where each solution is mixed with the same (constant) weight of adsorbent.
2. Mixing a batch of solutions, all containing the same initial solute concentration, with progressively increasing amounts of adsorbent.

The first technique obviously makes use of a single or constant soil: solution ratio, presumedly a standard ratio selected using the procedures given in Sections 9 or 10 and 17.8.3. The latter technique makes use of different soil:solution ratios in a manner very similar to the technique for selecting a soil: solution ratio for ionic solutes (Section 9). Intuitively, one would expect that either technique would yield the same result, and that either could be used. While these generalizations are true in some cases, they are not valid for all systems.

When using the constant soil:solution ratio technique, the initial or stock solute solution, albeit a solution prepared in the laboratory or a leachate taken from the field, is progressively diluted forming a batch of diluted solutions that are added to the containers, each with the same amount of soil material. However, as discussed in Section 11, the soil:solution ratio used may influence the adsorption data. Figure 22 showed that using different soil:solution ratios, ranging from 1:200 to 1:4 yielded adsorption data that were in poor agreement with the isotherm generated when a fixed (1:100) ratio was used. In this case, this phenomenon was attributed to competitive interactions between Cd^{2+}, and desorbed Ca^{2+} and Mg^{2+} and, as shown in Figure 23, where the data was replotted taking into account these competitive interactions, the adsorption data coalesced into a single consistent relationship. However, this replotting technique will not work in all cases. The techniques for modeling competitive adsorption are currently emerging (see for example, Murali and Aylmore, 1983 a, b, c; and Roy et al., 1986), and are currently too complicated for use in routine batch procedures. Moreover, not all "soil:solution ratio effects" can be attributed to competition (see Section 11). This dichotomy was characteristic of several of the soils and soil components used in developing these procedures; the application of the variable soil:solution ratio technique yielded results (amounts of cadmium and lead adsorbed) that were either similar to those using a fixed ratio or tended to be lower. On the basis of this trend, an isotherm produced using variable soil:solution ratios was viewed as the more environmentally conservative. Hence, an isotherm produced in this manner is called (in this document) an Environmentally Conservative Isotherm (ECI).

The Environmentally Conservative Isotherm (ECI)

The ECI has two major advantages over an isotherm where a fixed soil:solution ratio is used: 1) if the solute-adsorbent system reached equilibrium in 24 hours, or more correctly satisfied the conditions of the operational definition of equilibrium (Section 13), then the data generated in selecting a soil:solution ratio can be used to construct an isotherm, and 2) the effects of competition and other processes are implicitly accounted for without knowing their exact nature.

Further documentation that using a variable soil:solution ratio yields environmentally conservative estimates may be shown by Figure 33. The adsorption data were modeled with the Freundlich equation (Section 14) yielding the isotherm constants shown. The isotherms associated with the

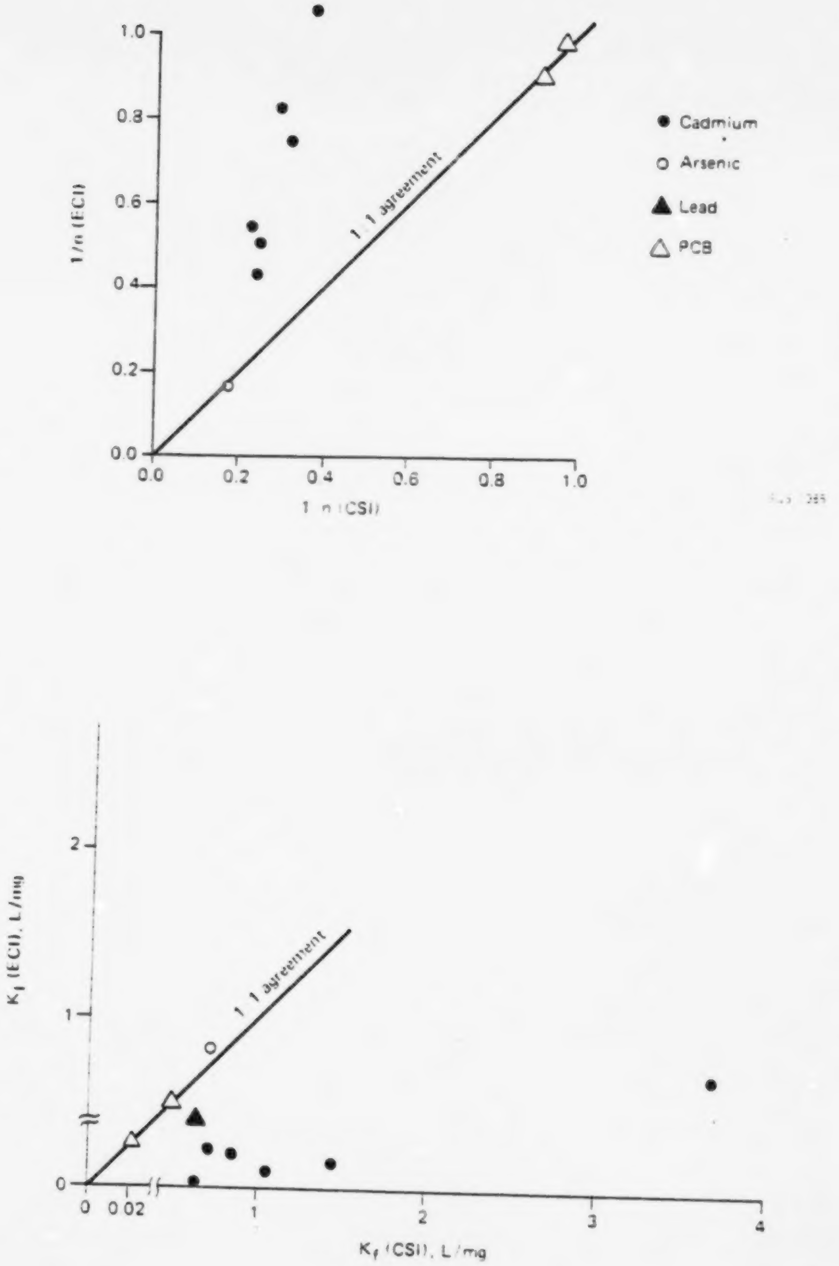

Figure 33. Distribution of (A) exponents (1/n) and (B) Freundlich constants (K_f) associated with arsenic, cadmium, lead, and PCB (Aroclor 1242) adsorption isotherms.

constant soil:solution ratio technique have been called Constant Soil:solution ratio Isotherms (CSI). The results shown in Figure 33 may be generalized as

$$K_f\ ECI < K_f\ CSI$$

and $$1/n_{ECI} > 1/n_{CSI}$$

and hence, based on this type of analysis, an isotherm generated using different adsorbent masses yields generally lower predictions of solute adsorption and was thus viewed as being environmentally conservative. The ECI is recommended as the method of choice in this document for routine use.

Experimental data produced during the process of selecting a soil:solution ratio may be used to construct an isotherm if the system equilibrated within 24 hours (equilibration time is discussed in the next section). However, it is inevitable that some of the data points will be associated with situations where less than 10% of the solute was adsorbed. In Section 9, it was recommended that one should choose a soil:solution ratio where at least 10% or greater adsorption occurred. To illustrate why this recommendation was made, consider a situation where an investigator conducted the experiments for selecting a soil:solution ratio then used data points from the entire concentration range regardless of the accuracy of the determination and attempted to construct adsorption isotherms (Figures 34 and 35). In each case shown, the data points that were associated with less than 10% adsorption did not conform to the general pattern established by the data associated with greater than 10% adsorption. Elimination of these data points yielded more satisfactory results, i.e., more reasonable r^2 values (see Section 14). Figure 35 represents an extreme case; nearly all of the data were associated with less than 10% adsorption. As shown, fitting this data set with an isotherm equation had little meaning.

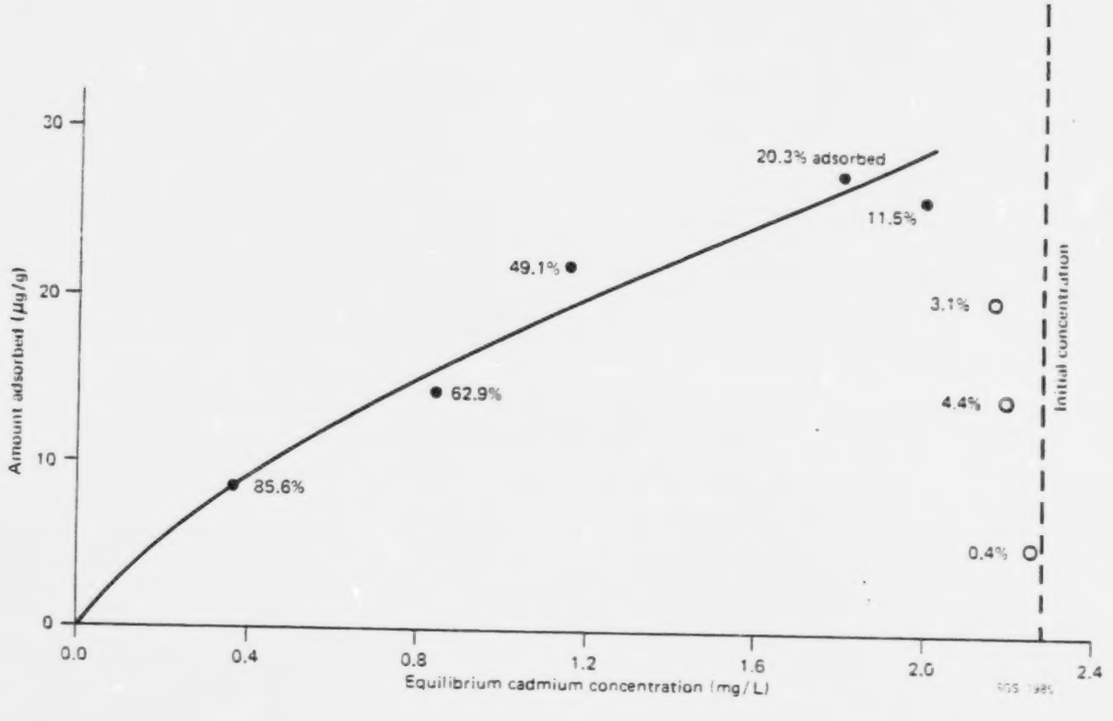

Figure 34. Cadmium adsorption isotherm at 22°C with a Vandalia till sample (unaltered) with the amount adsorbed associated with each isotherm data shown. The mean pH of the soil-solute suspensions was 6.8.

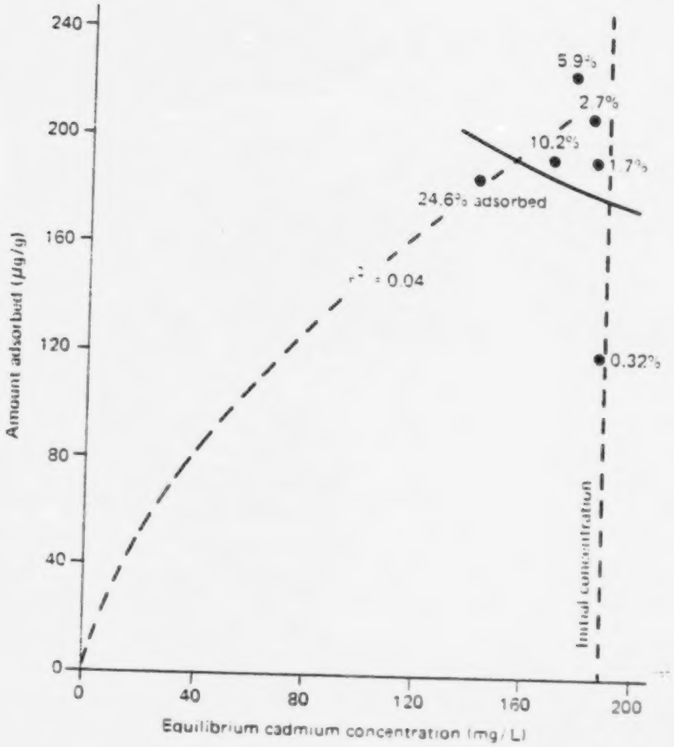

Figure 35. Distribution of cadmium adsorption data at 22°C by a Tifton sandy loam. The solid line is the Freundlich equation through the data; the dashed line is the presumed shape of the adsorption isotherm. The average pH of the soil-solute suspensions was 4.8.

While the ECI is useful for many situations, it can not be universally applied to every situation. The ECI may be limited to cases where (1) the adsorbent has a relatively high affinity for the solute, and (2) the initial solute concentration is relatively low. The ECI technique is often used with sparingly soluble organic solutes where the initial solute concentration is low.

The ECI technique was used to derive arsenic adsorption isotherms with the soil adsorbents used in the development of these procedures. Soil:solution ratios of 1:4 and higher were used, and the initial concentration of arsenic was 200 mg/L. Figure 36 illustrates the results; varying the amount of adsorbent over this range of soil:solution ratios did not change the equilibrium arsenic concentration substantially. The relatively small changes in arsenic equilibrium concentrations caused the data points to be somewhat clustered together, leaving an area between the origin of the isotherm and the lower-most arsenic equilibrium concentration without data points. It should be intuitively apparent that regression of these data sets using isotherm equations could lead to potentially large errors. Moreover, it was not possible to use lower soil:solution ratios to fill in the gaps; the use of ratios much less than 1:4 would eventually produce a very thick suspension or paste that could not be efficiently mixed, separated, or analyzed. This "ratio gap" problem is accentuated as the initial solute concentration increases; the "cluster" simply migrates to the right side of the isotherm. It is for these reasons that the constant soil:solution ratio isotherm (CSI) is also recommended for application as an alternate procedure, given that the (ECI) technique does not produce useful or applicable results. Such as the situation shown in Figure 36.

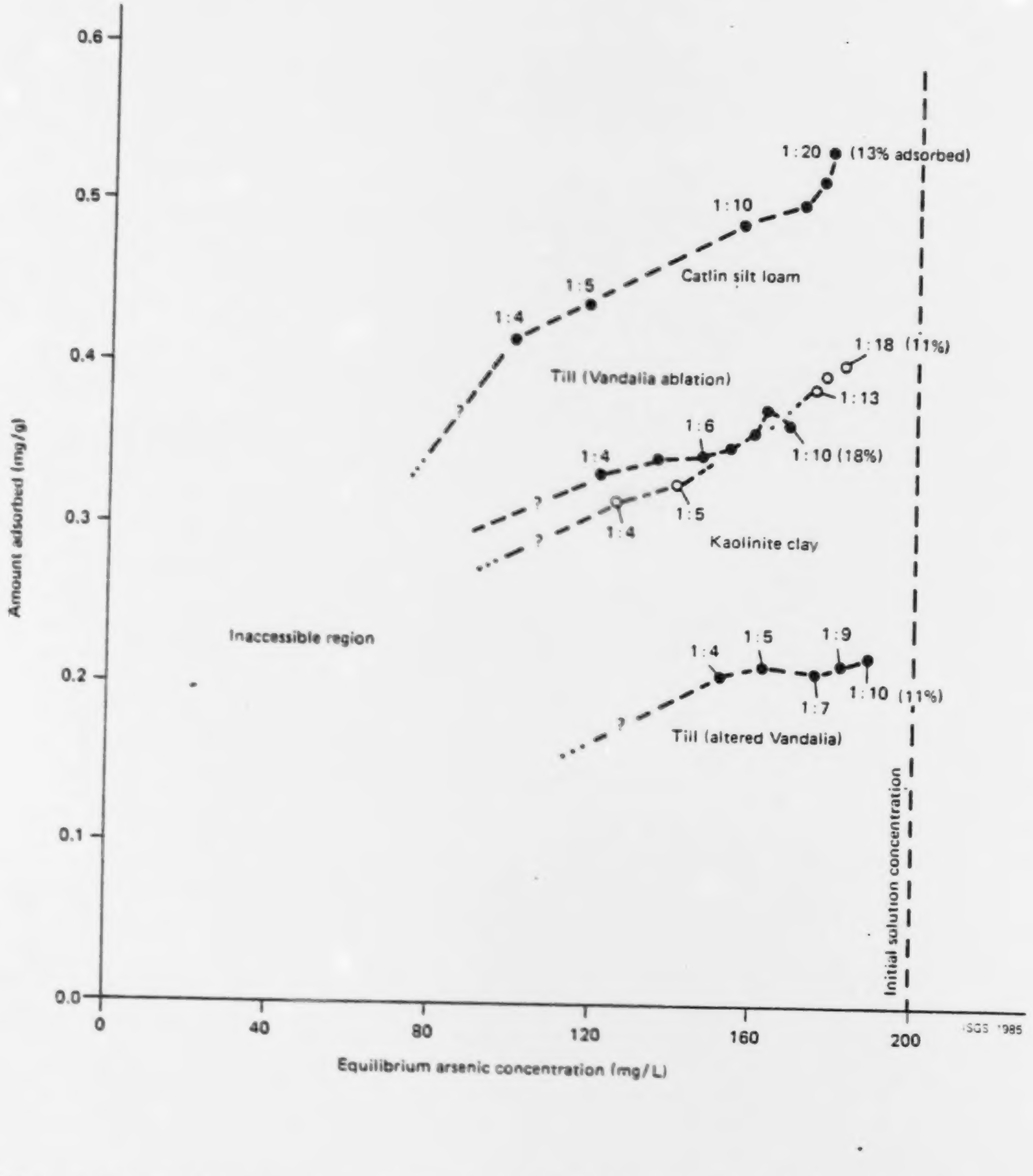

Figure 36. Distribution of arsenate adsorption data at 23°C by different soil samples using different soil:solution ratios. The pH values of each soil-solute system were similar to those given in Appendix A for each soil.

SECTION 13: DETERMINATION OF THE EQUILIBRATION TIME

The equilibration time in batch adsorption experiments is the time interval in which the system reaches chemical equilibrium and the concentrations of the products and reactants cease to change with respect to time, viz.,

$$\frac{\partial c}{\partial t} = 0 \qquad [13]$$

Adsorption at the solid-liquid interface is a thermodynamic process and adsorption measurements are taken when the system has equilibrated or, in other words, when the reaction(s) between the adsorbent and solute has gone to completion.

In past studies, many different equilibration times have been used. For example, Lawrence and Tosine (1976) used 30 minutes to equilibrate PCBs with soil, while Jones et al. (1979) allowed a soil-phosphate mixture to equilibrate for six days before separating the liquid from the soil. The equilibration times given in most studies were probably valid and were based on preliminary kinetic studies. However, there is a clear danger in assuming that the equilibration time reported by one investigator is valid for another system even though it is a similar adsorbent-solute system. Equilibration time is an experimental variable that must be determined for any system prior to undertaking the construction of an adsorption isotherm (curve).

The proposed ASTM 24-hour R_d procedure provides a measurement of the affinity of a soil or clay for solutes after 24 hours (Griffin et al., 1985). However, 24 hours may or may not be long enough for the development of chemical equilibrium. As indicated earlier, some investigators have used equilibration times of days or even weeks. However, adsorption *per se* is generally regarded as a fast reaction, and subsequent removal of a solute from solution may be attributed to other processes. Adsorption processes at solid-liquid interfaces are often initially rapid, while further reduction in solute concentration continues at a decreasing rate, asymptotically approaching a constant concentration. In some cases, equilibrium was never clearly attained. The ambiguity in the definition and measurement of equilibration times has been acknowledged as a major problem in adsorption studies (Anderson et al., 1981). For most systems involving complicated adsorbents such as soils, it is very difficult to determine when adsorption processes dominate then become less important as other processes, such as ion penetration or precipitation, become significant. The EPA (U.S. EPA, 1982) suggested that the equilibrium time should be the minimum amount of time needed to establish a rate of change of the solute concentration in solution equal to or less than 5% per 24-hour interval.

Thus this definition is an operational definition of equilibrium and is equivalent to a steady state. Cast in a form similar to that of eq. [13] it may be written as

$$\frac{\Delta C}{\Delta t} < 0.05 \text{ per 24-hour interval} \qquad [14]$$

The efficacy of this operational definition for equilibrium was evaluated using seven soil materials. Each of the adsorbents was exposed to arsenic and cadmium solutions, initially containing 200 mg/L, for periods of up to 72 hours. The solutions were analyzed and the rate of removal of the solute was determined. All of these particular soil-solute systems were found to be in equilibrium after 24 hours as defined by this operational definition. Figure 37 presents representative data for cadmium adsorption and Figure 38 shows the adsorption behavior of arsenate by 11 different soil materials. In this example, it is not obvious in some cases when the rate of change of the solute concentration is equal or less than 5% per 24-hour interval. It may be

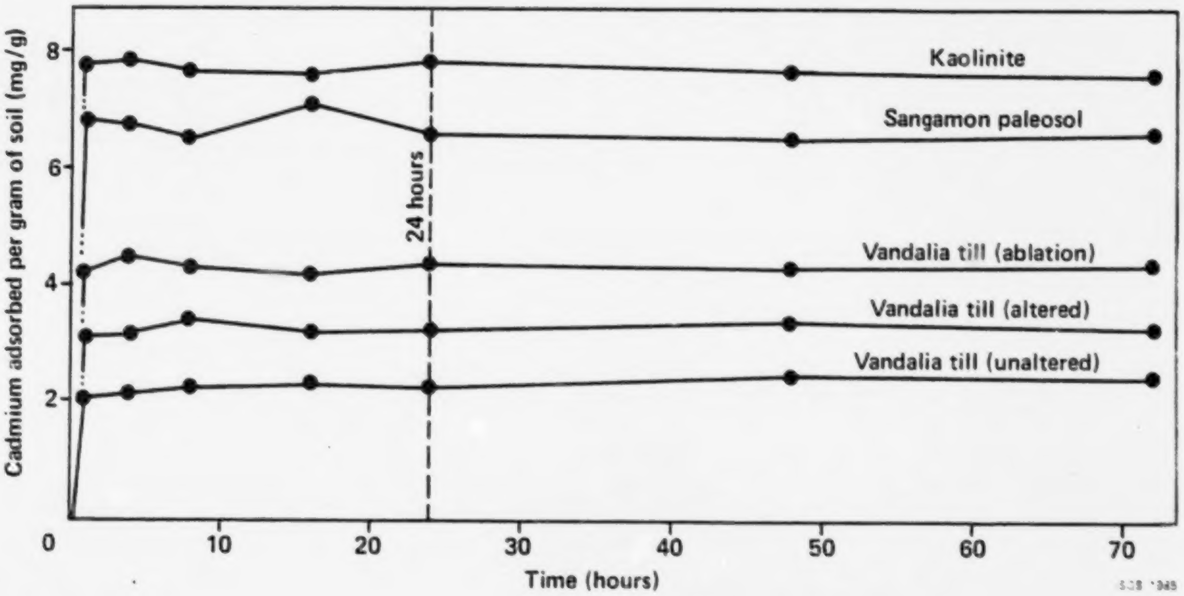

Figure 37. The adsorption behavior of cadmium by five soil materials at 22°C as a function of contact time.

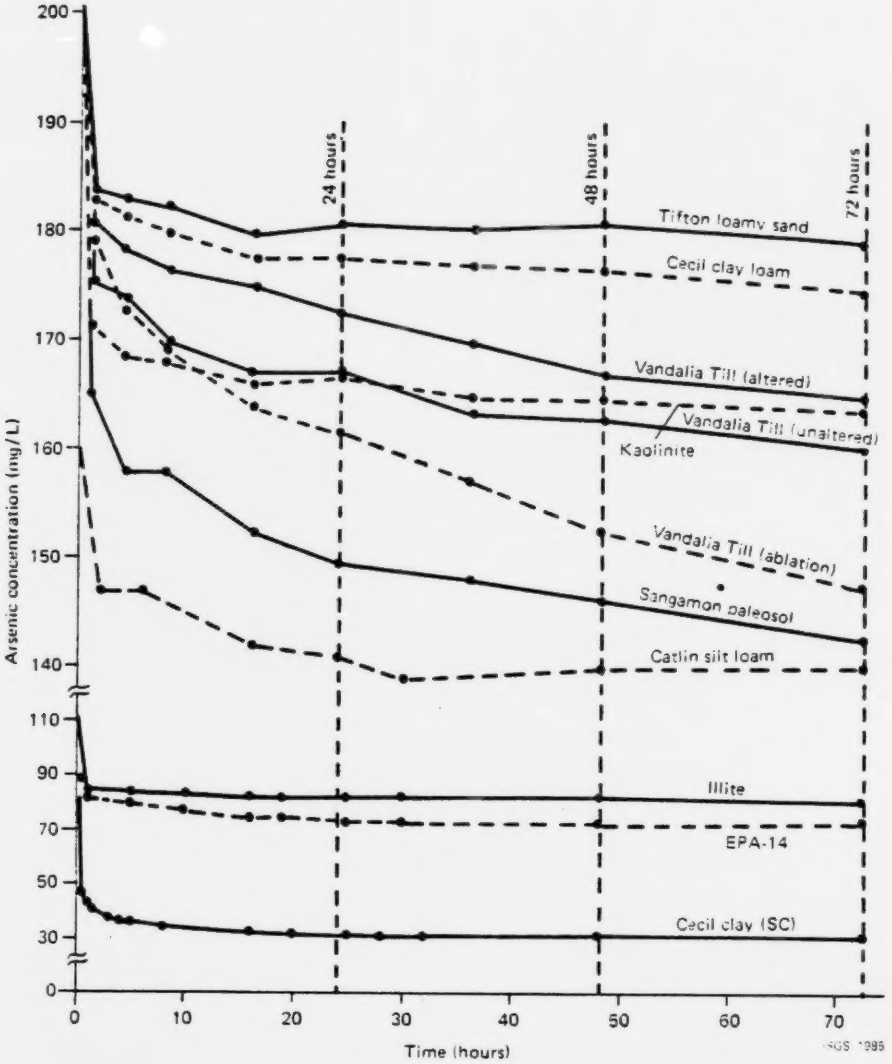

Figure 38. The adsorption behavior of arsenic at 23°C by 11 different soil materials as a function of contact time.

more convenient to analyze kinetic data in a manner shown in Table 10. As shown, an equilibration time of 24 hours was selected for three of the samples, while a period of 48 hours was used to equilibrate arsenate with a Vandalia till sample (ablation phase). In each example, the calculated %ΔC represents the change in concentration during the preceding 24 hours. After the first 24-hour interval, the amount of arsenic mixed with the kaolinite sample continued to decrease, but only by 1.14% during the next 24-hour interval. It is this slow and relatively small decrease in solute concentration which follows the more rapid and pronounced decrease that is frequently a problem. The application of this operational definition of equilibrium assumes that this additional 1.14% decrease is negligible and may be attributable to processes other than adsorption. Therefore, this solute-adsorbent system is defined as being at steady state after 24 hours of contact.

The application of this procedure with multicomponent solutions is exemplified by the metallic waste slurry (Appendix B). In order to determine the time interval necessary for the development of chemical equilibrium of each system, preliminary kinetic experiments were carried out using the soil: solution ratios previously determined (Section 9). Barium was adsorbed by the Sangamon paleosol sample and this system appeared to reach equilibrium within 24 hours. The rate of change in solute concentration for the first 24-hour period was 12.2% (Table 11). After 24 hours, the rate of change was less than 5 percent for each subsequent 24-hour interval. Similarly, the solution concentrations of lead and zinc were also constant after 24 hours (Fig. 39); "constant" in the sense that the rate of change in solution concentration of these two solutes per 24-hour interval was less than 5 percent (Table 11).

Table 10. Determination of equilibration times for the adsorption of arsenate by soil materials.

Cecil clay loam			Kaolinate		
Time (hr)	%ΔC[1]	Solution Conc. (mg/L)	Time (hr)	%ΔC	Solution Conc. (mg/L)
0	-	193.4	0	-	199.3
1	-	182.9	1	-	171.4
4	-	181.5	4	-	168.6
8	-	180.0	8	-	168.1
16	-	177.6	16	-	166.2
*24	8.17	177.6	*24	16.36	166.7
36	-	177.1	36	-	164.8
48	0.56	176.6	48	1.14	164.8
72	1.08	174.7	72	0.55	163.9

Vandalia Till (alation)			Sangamon Paleosol		
Time (hr)	%ΔC	Solution Conc. (mg/L)	Time (hr)	%ΔC	Solution Conc. (mg/L)
0	-	199.3	0	-	199.3
1	-	179.5	1	-	165.3
4	-	173.2	4	-	158.2
8	-	169.4	8	-	158.1
16	-	164.0	16	-	152.6
24	18.97	161.5	*24	33.13	149.7
36	-	157.3	36	-	148.3
*48	5.51	152.6	48	2.20	146.4
72	3.15	147.8	72	2.25	143.1

[1] $\%\Delta C = (C_1 - C_2)/C_1$ where C_1 = solution concentration at time t, and C_2 = the concentration at time t + 24 hours

* equilibration time selected for the adsorption isotherms

Table 11. Determination of equilibration times for the adsorption of Ba, Pb, and Zn from a Sandoval zinc slurry extract by the Sangamon paleosol and Cecil clay.

Time (hr)	%ΔC[1]	Solution Conc. (mg/L)	Time (hr)	%ΔC[1]	Solution Conc. (mg/L)
	- - - - Ba - - - -			- - - - Pb - - - -	
0	-	2.30	0	-	15.4
1	-	2.00	1	-	7.72
8	-	2.02	8	-	7.27
*24	12.2	2.02	24	54.5	7.01
31	-	2.02	31	-	6.72
48	-1.0	2.04	*48	6.3	6.57
72	-1.5	2.07	72	1.5	6.47
	- - - - Pb - - - -			- - - - Zn - - - -	
0	-	15.5	0	-	549
1	-	5.68	1	-	421
8	-	5.01	8	-	430
*24	66.8	5.14	*24	20.9	434
31	-	4.81	31	-	430
48	8.9	4.68	48	0.2	433
72	5.1	4.92	72	0.2	432
	- - - - Zn - - - -				
0	-	563			
1	-	387			
8	-	375			
*24	33.4	375			
31	-	371			
48	1.1	371			
72	0.3	370			

[1] %ΔC = $(C_1 - C_2)/C_1$ where C_1 = solution concentration at time t, and C^1_2 = concentration at time t + 24 hours

* equilibration time selected for the adsorption isotherms

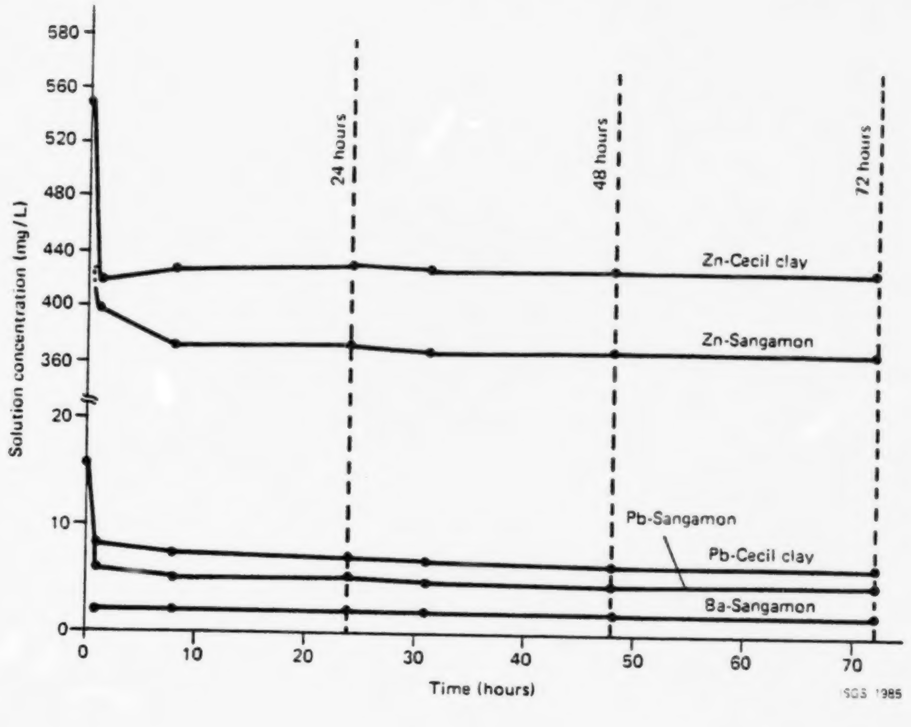

Figure 39. Determination of equilibration time of Ba, Pb, and Zn from a laboratory extract of the Sandoval Zinc slurry with the Sangamon Paleosol and the Cecil clay sample.

Zinc was adsorbed by the Cecil clay, and this system appeared to reach the operational equilibrium within 24 hours (Fig. 39). The rate of change in zinc concentration during the 24- to 48-hour interval was 0.2% (Table 11). Lead did not equilibrate with the Cecil clay until about 48 hours; the rate of change in lead concentration during the 48- to 72-hour interval was 1.5% (Table 11). Thus an equilibrium interval of 24 hours was used to construct adsorption isotherms with the exception of lead adsorption by the Cecil clay in which a 48-hour interval was used.

Solution concentrations of o-xylene, dichloroethane and tetrachloroethylene tended to change by amounts less than about 5% when in contact with Catlin (Fig. 40). As shown in Table 12, the rate of adsorption of the PCB Aroclor 1242 by a Catlin sample was nil after the initial 24 hours of contact.

● In summary, it is recommended that the equilibration time should be the minimum amount of time needed to establish a rate of change of the solute concentration in solution that is equal to or less than 5% per a 24-hour interval. This minimum time, typically 24 hours, should be determined for each solute-adsorbent system prior to the construction of adsorption isotherms.

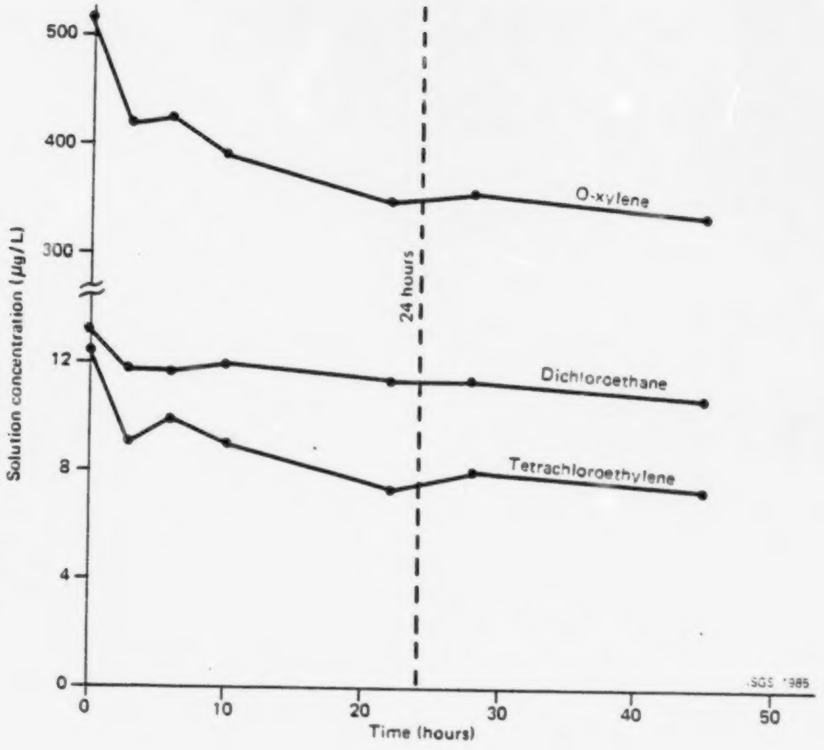

Figure 40. The adsorption behavior of o-xylene, dichloroethane, and tetrachloroethylene at 23°C by Catlin as a function of contact time, at pH 6.1.

Table 12. Determination of equilibration time for the adsorption of the PCB Aroclor 1242 by Catlin.

Time (hr)	%ΔC	Solution conc. (mg/L)
0	-	0.220
2	-	0.020
4	-	0.018
6	-	0.017
8	-	0.017
*24	94.31	0.013
48	0.00	0.013

* Equilibration time selected for an adsorption isotherm.

SECTION 14: CONSTRUCTION OF ADSORPTION ISOTHERMS (CURVES)

An adsorption isotherm or curve is a graphical representation that shows the amount of solute adsorbed by an adsorbent as a function of the equilibrium concentration of the solute. This relationship is quantitatively defined by some type of partition function or adsorption isotherm equation that is statistically applied to the adsorption data in order to generalize the adsorption data.

In studies concerned with the adsorption of gases by solids, over 40 different equations have been used to describe the data. Historically, only a few of the equations have been found to be applicable to solid-liquid systems. Only the most commonly used and simplest of these adsorption equations will be discussed here.

THE FREUNDLICH EQUATION

Probably the oldest known adsorption equation that has been widely used for solid-liquid systems is the Freundlich adsorption equation, viz.,

$$\frac{x}{m} = K_f C^{1/n} \qquad [15]$$

where x is the amount or concentration of the solute adsorbed, m is the mass of the adsorbent, C is the equilibrium concentration of the solute, and K_f and $1/n$ are constants.

Freundlich (1909) used this expression extensively, but it was first proposed by van Bemmelen in 1888. The Freundlich equation was originally proposed as an empirical expression without a theoretical foundation. However, some investigators have referred to the Freundlich constant K_f as being related to the capacity or affinity of the adsorbent and the exponential term as an indicator of the intensity, or how the capacity of the adsorbent varies with the equilibrium solute concentration (various references cited in Suffet and McGuire, 1980).

Other investigations have attempted to show that the Freundlich equation has a theoretical basis. A number of derivations of the Freundlich equation were based on the Gibbs adsorption equation (Chakravarti and Dhar, 1927; Rideal, 1930; Freundlich, 1930 and Halsey and Taylor, 1947; see also Hayward and Trapnell, 1964, and Kipling, 1965). Zeldowitsch (1935) demonstrated that the Freundlich equation could be explained in terms of a non-homogeneous surface. Sips (1948) established in a rigorous fashion a general relationship between surface heterogeneity and the Freundlich equation, a derivation Sposito (1980) partially adapted to his system to derive a Freundlich-type expression for trace-level exchange reactions.

The Freundlich equation is an often used expression, probably because of its ease of application: it contains two constants that are both positive-valued numbers that may be statistically solved when the expression is cast in the logarithmic form, viz.,

$$\log(x/m) = \log K_f + {}^1/n \log C \qquad [16]$$

By taking the logarithms of both sides of eq. [15], the constants K_f and ${}^1/n$ may be solved, via eq. [16], as a simple linear regression. The following example is given to illustrate the application of the Freundlich equation.

From previous work, it was determined that the adsorption of arsenate by kaolinite could be characterized by using a 1:10 soil:solution ratio (Section 9), and that the system reached a steady state after 24 hours. Using these experimental conditions, 17 dilutions of a stock KH_2AsO_4 solution were mixed with an NBS rotary extractor with kaolinite for 24 hours. Table 13 contains all the data needed to construct an isotherm, as well as the individual pH and electrical conductivity (EC) of each solution as recommended at the end of Sections 5 and 6.

Table 13. Data reduction for arsenic adsorption at 25°C by a kaolinite clay sample. The volume of solution was 200 mL

Initial concentration (mg/L)	Equilibrium concentration (mg/L)	Adsorbent weight (g)	Amount adsorbed (x/m) as μg/g	pH	EC (dS/m)
4.89	1.20	20.42	36*	8.30	160
10.0	3.56	20.42	64	8.26	168
15.2	6.78	20.42	84	8.26	170
19.9	10.1	20.42	98	8.19	185
19.9	10.1	20.42	98	8.23	185
19.9	10.3	20.42	96	8.25	185
29.9	17.6	20.42	123	8.16	205
40.3	25.0	20.42	153	8.03	221
49.4	33.4	20.42	160	8.02	240
80.5	58.4	20.42	221	7.77	305
80.5	59.5	20.42	210	7.80	313
80.5	58.9	20.42	216	7.83	305
98.8	76.3	20.42	225	7.69	350
121.0	92.6	20.42	284	7.56	385
137.7	109.4	20.42	283	7.50	413
160.3	128.3	20.42	320	7.27	434
160.3	129.7	20.42	306	7.26	430

* sample calculation:

$$\frac{x}{m} = \frac{(\text{Initial conc. - equil. conc.}) \times \text{volume of solution}}{\text{weight of adsorbent}}$$

$$= \frac{(4.89\ \text{mg/L} - 1.20\ \text{mg/L}) \times 0.200\text{L}}{20.42\ \text{g}} = 0.036\ \text{mg/g} = 36\ \mu\text{g/g}$$

As indicated earlier, the Freundlich equation may be solved when cast in a logarithmic form that is equivalent to a simple linear regression, viz.,

$$y_i = a + bx_i \qquad [17]$$

$$\begin{aligned} \text{where } \log(x/m)_i &= y_i \\ \log K_f &= a \\ {}^1/n &= b \\ \log C_i &= x_i \end{aligned}$$

The technique for solving a linear regression may be found in any introductory statistics text, and is also a common feature of most intermediate-priced electronic calculators. (Note that linear regressions are sometimes referred to as the line of best fit, or method of least squares.) However, for the sake of completeness, the constants may be solved using

$$b = \frac{1}{n} = \left(\frac{n^* \left(\Sigma \log C_i \times \log x/m_i\right) - \left(\Sigma \log C_i\right)\left(\Sigma \log x/m_i\right)}{n^* \left(\Sigma(\log C_i)^2\right) - \left(\Sigma \log C_i\right)^2}\right) \qquad [18]$$

$$\log K_f = \frac{\Sigma \log \frac{x}{m_i}}{n^*} - \left(\frac{1}{n}\right) \frac{\Sigma \log C_i}{n^*}$$

where n^* is the number of pairs of data points.

In this example (Table 13)

$$\text{Log } K_f = 1.536 \qquad {}^1/n = 0.452$$

and thus,

$$\frac{x}{m} = 34.328\ (\text{As})^{0.452} \qquad [19]$$

where (As) is the equilibrium concentration of arsenic in solution (mg/L).

Thus, eq. [19] becomes a predictive equation capable of describing the adsorption data. The reader may wish to use the data given in Table 13 to verify eq. [19].

Eq. [19] will statistically predict solute-adsorbate partitioning over an equilibrium concentration range of 0 to approximately 130 mg As/L. This expression (eq. [19]), as well as any Freundlich expression, should never be extrapolated beyond the experimental range used in its construction. In other words, eq. [19] should not be used to predict x/m at equilibrium concentrations greater than 130 mg/L; to do so will require the collection of data in this higher concentration range. The validity of this cautionary note becomes apparent when one considers that the Freundlich equation predicts infinite adsorption at infinite concentrations, and hence that any soil or clay would have an unlimited capacity to retain chemicals dissolved in water. Not only would an infinite capacity be thermodynamically inconsistent, experience has shown that the extent of adsorption is ultimately limited by the surface area (or some portion of the surface) of the adsorbent. Thus, there are two drawbacks with respect to using the Freundlich equation: (1) it cannot be extrapolated with confidence beyond the experimental range used in its construction, and (2) it will not yield a maximum capacity term which in many cases is a convenient single-valued number that estimates the maximum amount of adsorption beyond which the soil or clay is saturated and no further net adsorption can be expected.

THE LANGMUIR EQUATION

The Langmuir equation has given rise to a number of Langmuir-type expressions that have been widely used to describe adsorption data for solid-liquid systems. The most commonly-used expression may be generalized as

$$\frac{x}{m} = \frac{K_L MC}{1 + K_L C} \qquad [20]$$

where x is the amount or concentration of the solute adsorbed, m is the mass of the adsorbent, C is the equilibrium concentration of the solute, and K_L and M are constants.

Langmuir (1918) derived an expression similar to eq. [20] to describe the adsorption of gases on solids (flat surfaces of glass, mica, and platinum). He generalized that the Freundlich equation was unable to describe the adsorption of gases when the range of pressures was large.

Langmuir's original derivation was based on the premise that during the adsorption of gases, a dynamic equilibrium is established where the rate of condensation (adsorption) is equal to the rate of evaporation (desorption). Derivations of the Langmuir and Langmuir-type equations for gas-solid interactions are given elsewhere (Langmuir, 1918, Hayward and Trapnell, 1964; and Ponec et al., 1974). Langmuir-type expressions for ion exchange reactions in soils have also been derived (Sposito, 1979; and Elprince and Sposito, 1981).

The applicability of Langmuir-type equations in solid-liquid systems has been a controversial topic in recent years (see Harter and Baker, 1977; Veith and Sposito, 1977; Barrow, 1978; and Sposito, 1982). However, this controversy is concerned with interpretations with respect to adsorption mechanisms and energetics based on the results of applying Langmuir-type expressions rather than the ability of the equation to simply describe the adsorption data.

It appears to be the general consensus of several investigators that the Langmuir constant (K_L) is somehow related to the bonding energy between the adsorbed ion and the adsorbent but the specific functional relationship is uncertain. The constant M in eq. [20] is also generally accepted as the adsorption maximum of the adsorbent with respect to the specific solute, and it is interpreted as the maximum amount or concentration that an adsorbent can retain.

Langmuir-type equations are often used because of their ease of application. Like the Freundlich equation, it contains only two constants that are both positive-valued numbers that may be statistically solved when eq. [20] is cast in a linear form. Two linearized expressions are possible:

$$\frac{C}{x/m} = \frac{1}{K_L M} + \frac{C}{M} \qquad [21]$$

$$\frac{1}{x/m} = \frac{1}{K_L MC} + \frac{1}{M} \qquad [22]$$

The linearized form of eq. [21] is sometimes referred to as the "traditional linear Langmuir equation," while eq. [22] is called the "double-reciprocal Langmuir equation." The latter is more suitable to situations where the distribution of equilibrium concentrations tends to be skewed towards the lower end of the range of the equilibrium concentrations.

As indicated above, linearized Langmuir-type expressions such as eqs. [21] and [22] are equivalent to a simple linear regression, viz.,

$$y_i = a + bx_i \qquad [17]$$

whereas in the case of the traditional linear Langmuir equation

$y_i = (C/x/m)_i$

$a = 1/K_L M$

$b = 1/M$

$x_i = C_i$

and in the case of the double-reciprocal form

$y_i = (1/x/m)_i$

$a = 1/M$

$b = 1/K_L M$

$x_i = 1/C_i$

The techniques for solving either eqs. [21] or [22] are the same as those applied to solve the linear form of the Freundlich equation (eq. [16]). Using the data set given in Table 13, applying the linear Langmuir-type equations yields:

Traditional Linear Langmuir:

$$a = \frac{1}{K_L M} = 0.0792 \qquad [23]$$

$$b = \frac{1}{M} = 0.0028 \qquad [24]$$

and thus

$$\frac{x}{m} = \frac{3.568 \times 10^{-2}\ (353.856)\ C}{1 + 3.568 \times 10^{-2}\ (C)} \qquad [25]$$

Double-Reciprocal Plot:

$$a = \frac{1}{M} = 0.0050 \qquad [26]$$

$$b = \frac{1}{K_L M} = 0.0297 \qquad [27]$$

and thus,

$$\frac{x}{m} = \frac{0.1702\ (198.098)C}{1 + 0.1702(C)} \qquad [28]$$

Thus, eqs. [25] and [28] are also predictive expressions capable of describing the adsorption of arsenic by kaolinite. The reader should also work through these examples to verify the results.

SECTION 15: SELECTION OF ADSORPTION EQUATIONS

In brief, there are three isotherm regressions to describe the example data set given in Table 12. However, given the selection of different equations, usually one of the equations will describe the results with the greatest accuracy. In terms of simply fitting adsorption data, there appears to be no clear consensus as to which equation (Freundlich or Langmuir-type) generally is most reliable. Barrow (1978) objected to the application of Langmuir-type expressions, but his objection was based on theoretical considerations. Singh (1984) compared five adsorption equations and found that the Freundlich equation was the most accurate in describing the adsorption of SO_4^{2-} by soils. Polyzopoulos et al. (1984) compared four adsorption equations in a study concerned with phosphate adsorption by soil. They found that either a Langmuir-type or Freundlich expression could describe the data with comparable success.

Generally the choice among equations is based on the coefficient of determination (r^2) obtained in a given case along with a given equation's simplicity in form (Polyzopoulos et al., 1984). The Freundlich and Langmuir equations both contain only two constants and are both easily solved.

The coefficient of determination (sometimes called the "goodness of fit") is a measure of how closely the regression line fits that data, and may be calculated using eq. [29]:

$$r^2 = \frac{\Sigma\,(\dot{y}_i - \bar{y})^2}{\Sigma\,(y_i - \bar{y})^2} \qquad [29]$$

where $\dot{y}_i$ is the value of the dependent variable predicted by the regression, y_i is the value actually measured, and $\bar{y}$ is the arithmetic mean of all y_i. The value of r^2 will always be between zero and one, inclusive. If all of the points are close to the regression line or, in this case, if all of the adsorption data plot closely to the statistically-constructed adsorption isotherm, the corresponding r^2 will be close to one. The application of eqs. [16], [21], and [22] to the data set given in Table 12 yielded dissimilar r^2 values:

Freundlich	0.996
traditional linear Langmuir	0.954
double-reciprocal Langmuir	0.916

Using the coefficient of determination as a criterion, the Freundlich equation best describes the adsorption data although the traditional linear Langmuir expression would also yield satisfactory results. Inspection of Figure 41 clearly shows that the double-reciprocal linear Langmuir equation did not fit the adsorption data well, while the traditional linear form tended to overpredict adsorption in the upper part of the isotherm. Obviously the high r^2 value associated with the Freundlich equation is reflected by the closeness of fit of the isotherm with the data.

Obtaining a reliable "fit" of adsorption data with the chosen equation such that r^2 values are close to one is a major concern when constructing adsorption isotherms. However, it is inevitable that in some cases a low r^2 value may be obtained regardless of the equation used giving rise to concerns that the adsorption constants have little meaning. Probably the simplest statistical test that can be used in these situations is to use t-statistics to examine whether the sample correlation coefficient (r) is significantly different from a population correlation coefficient (ρ) where $\rho = 0$. This test should be given in most introductory statistics text books and will not be discussed here.

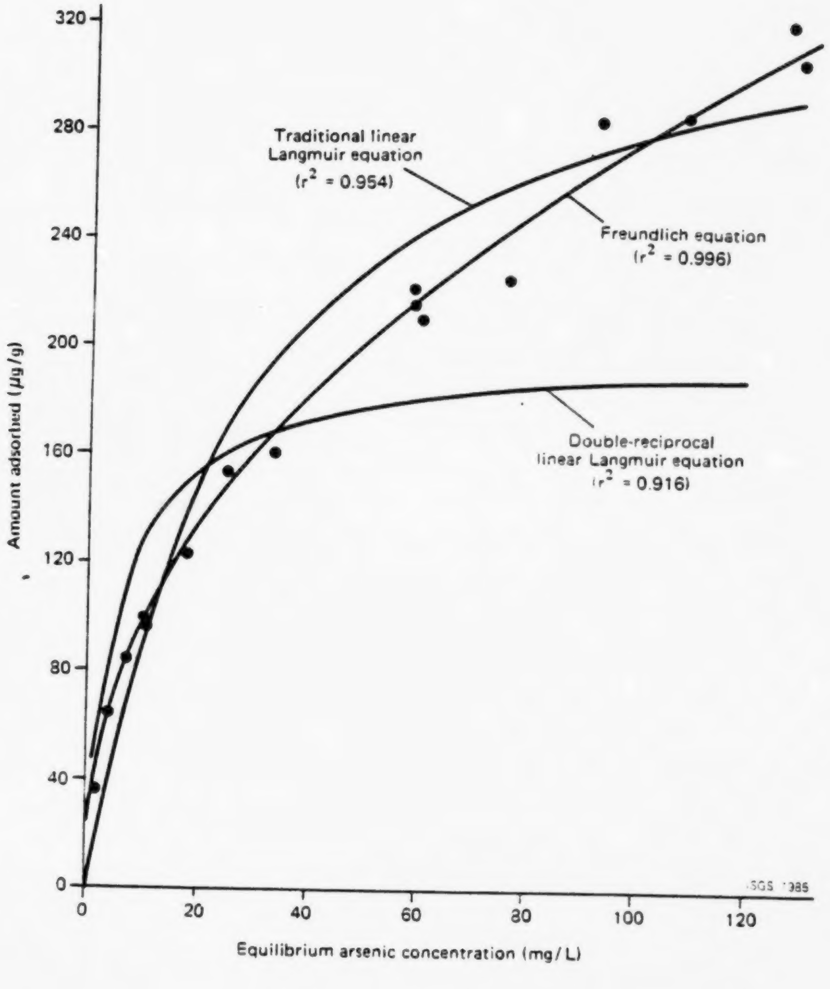

Figure 41. The adsorption of arsenic by a kaolinite clay sample at 25°C as described by the traditional linear Langmuir, double-reciprocal Langmuir, and the Freundlich Equation. The mean pH of the soil-solute suspensions was 7.8.

SECTION 16: APPLICATION OF BATCH ADSORPTION DATA

This section was included to serve as a brief introduction to the application of batch adsorption data in calculations of solute movement through compacted landfill liners, particularly for estimating the minimum thickness of liner required to prevent pollutant movement beyond a certain depth for a specified period of time. As leachate moves through a liner, the movement of chemical solutes in the leachate may be retarded if adsorbed by the liner. We may define R as the ratio of the velocity of the leachate to that of the solute, viz.,

$$R \equiv V_{leachate}/V_{solute} \qquad [30]$$

The R term is called the retardation function or factor. When the solute is not retained by the liner, R equals one; the solute moves at the same velocity as the leachate. Increasing degrees of adsorption yield larger values for R.

The retardation factor may also be defined by an empirical relationship (Freeze and Cherry, 1979 and references cited therein) as

$$R = 1 + \frac{\rho_b(K_d)}{\theta} \qquad [31]$$

where ρ_b is the dry bulk density of the liner

K_d is a distribution coefficient, and

θ is the volumetric water content of the liner.

The distribution coefficient is a parameter that describes the partitioning of solutes between the leachate and the liner soil materials at equilibrium. The distribution coefficent may be defined as

$$\frac{dS}{dC} \equiv K_d \qquad [32]$$

where S is equal to x/m (the amount adsorbed per mass of adsorbent), and

C is the equilibrium concentration of the solute.

In other words, eq [32] is the slope of an adsorption isotherm.

In order to use eq. [31], a functional relationship for dS/dC must be determined. The possible solutions range from simple assumptions to complex numerical solutions. The simplest case is where the adsorption of the solute conforms to a Freundlich equation (Section 14) isotherm where the $^1/n$ term is unity, viz

$$\frac{x}{m} = S = K_f C^{1/n} = K_f C \qquad [33]$$

Such an isotherm is termed linear; a plot of S versus C is a straight line. The slope of this type of plot yields K_d;

$$\frac{dS}{dC} = K_f \text{ or } K_d \qquad [34]$$

$$\text{hence,} \quad R = 1 + \frac{\rho_b K_d}{\theta} \qquad [35]$$

In the case of a linear isotherm, the Freundlich constant (K_f) reduces to the simple partition constant (K_d), a single-valued number that is used to calculate solute-adsorbate partitioning at any equilibrium concentration of the solute. Because of its mathematical simplicity, this approach (the linear isotherm assumption) has been widely used and may be valid for many dilute systems. When the adsorption isotherm of a solute is a nonlinear function ($^1/n \neq 1$), the retardation factor is concentration-dependent:

$$\frac{dS}{dC} = \frac{d}{dC}\left(K_f C^{1/n}\right) = \frac{K_f}{n} C^{1/n - 1} \qquad [36]$$

$$\text{hence,} \quad R(C) = 1 + \frac{\rho_b K_f C^{1/n - 1}}{\theta n} \qquad [37]$$

Eq. [37] is complicated by the fact that the numerical value of R will depend on the concentration of the solute. Solute movement may be seriously underestimated by assuming that a constant retardation factor is valid for a given system when dealing with nonlinear isotherms. Rao (1974) proposed an empirical estimation technique to solve eq. [37] which may be written as

$$\bar{R} = 1 + \frac{\rho_b K_f Co^{1/n - 1}}{\theta} \qquad [38]$$

where $\bar{R}$ is a weighted-mean value and Co is the highest initial (before contact with the adsorbent) concentration of the solute.

In a study concerned with pesticide adsorption by a soil sample, Davidson et al. (1976) found that the error introduced by assuming linear adsorption isotherms was not serious at low concentrations (< 10mg/L) but becomes significant at higher concentrations. Van Genuchten et al. (1977) proposed an alternative method for isotherm linearization that the reader may wish to examine.

In order to demonstrate possible applications of these concepts, the following examples are presented to illustrate how batch adsorption data are used to estimate clay liner thickness.

In this hypothetical example, the metallic waste described in Appendix B is to be placed into a disposal basin that has been lined with Cecil clay loam (refer to Appendix A). The soil has been graded, blended, and compacted and has a saturated hydraulic conductivity of 10^{-7}cm/sec. The major concern of the company operating the disposal facility is the possible uncontrolled movement of a leachate plume containing high concentrations of lead in solution. In a preliminary analysis, this company conducted batch adsorption experiments using a $Pb(NO_3)_2$ salt, and samples of the Cecil soil (Table 14). The question that is posed is that for a 5-year operating life and a 30-year post-closure period, what is the minimum thickness that the liner must be in order to attenuate the lead from solution?

There are several approaches that may be used to answer this question. For each approach, the mean pore velocity of the leachate through the liner must be calculated, and this may be done using Darcy's Law as

$$V = K_{sat} i / n_e \qquad [39]$$

where K_{sat} is the saturated hydraulic conductivity of the liner,
i is the hydraulic gradient (dH/dZ), and
n_e is the effective (water conducting) porosity of the liner.

If we assume saturated conditions, subjected to steady state flow through an isotropic liner over times t, and neglect the effects of dispersion and diffusion, eq. [39] can be combined with eq. [31] to yield

$$Z = t\, K_{sat}\, i / R\, n_e \qquad [40]$$

where Z is the estimated vertical distance of migration of the solute (in cm),
t is time in seconds, and all other variables have been defined previously.

Eq. [40] treats solute movement as a piston-flow problem; a chemically uniform slug of leachate moving downward. This expression is simple, and may readily be used to estimate the minimum thickness of a liner. To simplify its application, it is often assumed that the isotherm is linear. In this example (Table 14 and Figure 42), a linear regression of the data through the origin (Steel and Torrie, 1960) yielded

Table 14. Lead adsorption data using a $Pb(NO_3)_2$ salt and the Cecil clay. The volume of solution was 200 mL and the adsorbent weight was 10.18 grams.

Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Amount Adsorbed (x/m) as µg/g	pH	EC (dS/m)
2.07	0.05	61	4.79	27
5.11	0.11	100	4.74	33
5.11	0.11	100	4.75	35
6.22	0.16	121	4.74	34
7.28	0.22	141	4.73	33
10.2	0.41	196	4.68	39
10.2	0.43	195	4.67	40
12.4	0.65	235	4.66	45
14.6	0.94	273	4.62	45
14.6	0.94	273	4.62	43

$$\frac{x}{m} = S = 342(Pb)$$

Moreover, it is assumed that the liner has the following properties:

$$n_e = 0.09\ cm^3/cm^3$$

$$\theta = 0.36\ cm^3/cm^3$$

$$\rho_b = 1.7\ g/cm^3$$

$$K_{sat} = 1 \times 10^{-7} cm/sec$$

$$i = dH/dz = 1\ cm/cm$$

and

$$35\ years = 1.1038\ x10^9\ seconds.$$

With these assumptions, the retardation factor becomes

$$R = 1 + \frac{1.7(342)}{0.36} = 1619$$

and solving eq. [40] becomes

$$Z = (1.1038 \times 10^9)(1 \times 10^{-7})\ (1)/1619(0.09)$$

$$Z = 0.8\ cm$$

Thus, based on this approach, the compacted liner would have to have a minimum thickness of only about 1 cm to attenuate lead over a 35-year period. However, while the application of a linear isotherm yields a reasonable coefficient of determination ($r^2 = 0.95$), inspection of Figure 42 indicates that this approach over-estimates lead adsorption at high lead concentrations, and underestimates adsorption at lower concentrations. The adsorption of lead (Table 14) is more accurately described by a Freundlich equation;

$$\frac{x}{m} = S = 291(Pb)^{0.492}$$

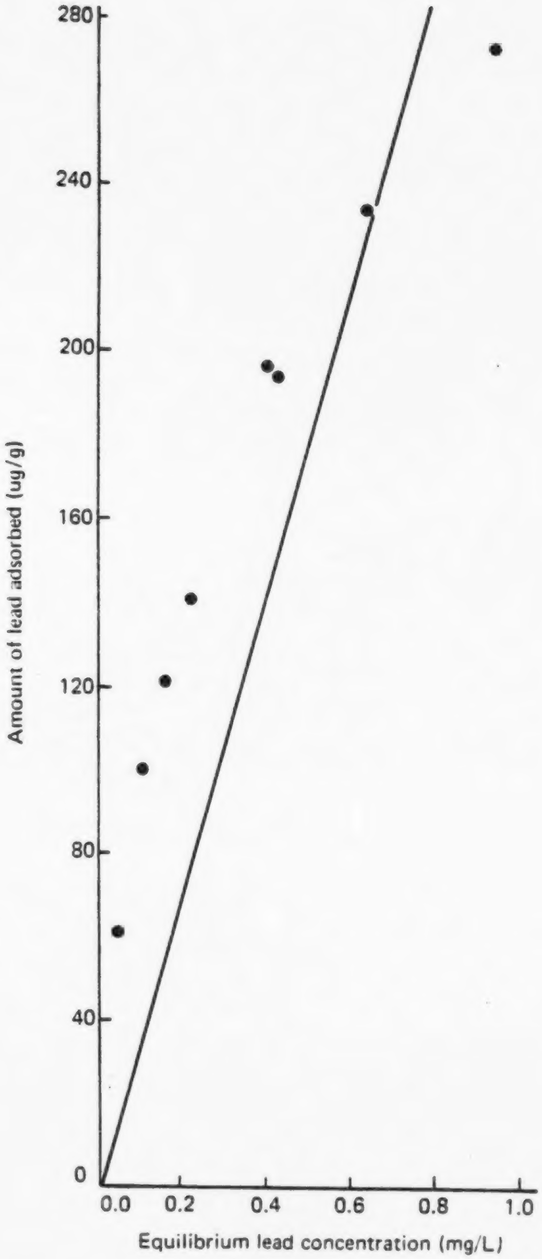

Figure 42. Lead adsorption by Cecil clay loam at pH 4.5, and at 25°C described by a linear Freundlich equation through the origin.

As a second level of refinement, the nonlinearity of the isotherm is considered using eq [38] to estimate a weighted-mean retardation factor (Davidson et al., 1976). An appropriate value for Co was determined from a laboratory extract of the metallic waste sample (Appendix B) which suggested that the maximum amount of lead that will initially come in contact with the liner is approximately 15 mg/L Pb. Making use of eq. [38], a revised retardation factor becomes

$$\bar{R} = 1 + \frac{1.7(291)15^{(0.492-1)}}{0.36}$$

$$= 348$$

and the minimum thickness, based on the weighted-mean retardation factor is

$$Z = (1.1038 \times 10^{9})(1 \times 10^{-7})(1)/348(0.09)$$

$$= 3.5 \text{ cm}$$

Consequently by considering the nonlinearlity of the isotherm, the minimum thickness of the liner is estimated to be about 4 cm.

As a third level of refinement, the chemical composition of the leachate was considered. The first two estimates were based on lead adsorption from a pure $Pb(NO_3)_2$ solution. Laboratory extracts of the waste also contained large concentrations of zinc (Appendix B). The adsorption of lead from the extract was found to be significantly less than that from the pure $Pb(NO_3)_2$ solution, presumably due to competitive interactions between Zn^{2+} and Pb^{2+} for adsorption sites. The net effect is that lead is more mobile in the presence of zinc. The adsorption of lead by Cecil from the laboratory extract of the waste was found experimentally to be described by:

$$\frac{x}{m} = S = 70\ (Pb)^{0.481}$$

If the minimum liner thickness is recalculated using these isotherm constants and eqs. [38] and [40], the thickness is estimated to be about 15 cm, again assuming that the initial lead concentration in the leachate is 15 mg/L. Clearly, migration distance estimates based on adsorption data using pure, single-solute data may underestimate the minimum thickness of liners because they fail to account for competitive interactions which may significantly reduce adsorption.

At the next level in refining the estimated liner thickness, the effects of dispersion and diffusion are considered. In saturated homogeneous materials that are subjected to steady-state flow conditions along a flow path z, the change in solute concentration as a function of time may be generalized (Ogata, 1970; Bear, 1972; Boast, 1973; and Freeze and Cherry, 1979) as

$$\frac{\partial C}{\partial t} = D_z \frac{\partial C^2}{\partial z^2} - \bar{V}_z \frac{\partial C}{\partial z} - \frac{\rho_b}{\theta} \frac{\partial S}{\partial t} \qquad [41]$$

where C is the concentration of the solute,

D_z is the effective diffusion-dispersion coefficient (distance ^{2}/time) along the flow path z,

$\bar{V}_z$ is the mean convective flow velocity (distance/time) along the flow path z,

ρ_b is the bulk density (weight/volume) of the material,

θ is the volumetric water content (vol./vol.),

S is the amount of solute adsorbed per mass of adsorbent (x/m), and

t is time.

Eq. [41] may be rearranged as

$$R \frac{\partial C}{\partial t} = D_z \frac{\partial C^2}{\partial z^2} - \bar{V}_z \frac{\partial C}{\partial z} \qquad [42]$$

where R is the retardation factor.

The analytical solution to this second-order differential equation (Ogata, 1970) is given by

$$\frac{C}{Co} = \frac{1}{2}\left[\mathrm{erfc}\left(\frac{z - Vt^*}{2(D_z t^*)^{0.5}}\right) + \exp\left(\frac{Vz}{D_z}\right)\mathrm{erfc}\left(\frac{z + Vt^*}{2(D_z t^*)^{0.5}}\right)\right] \qquad [43]$$

where C/Co is the ratio of the solute concentration at time t and distance z to the initial solute concentration, Co;

erfc is the complementary error function,

V is the average linear pore water velocity (cm/sec),

D_z is the vertical dispersion coefficient (cm^2/sec),

t* is the retarded time (actual time divided by the retardation factor R or $\bar{R}$),

and z is vertical distance of migration (cm),

furthermore,

$D_z = \alpha V + D^*$ where α is the dispersivity (cm) and D* is the diffusion coefficient in water (cm^2/sec).

In the following examples, the three previous liner thickness estimations were recalculated using eq. [43]. The only additional information needed to conduct this analysis was to assign a value to the dispersivity. The dispersivity (α) has been found to be scale dependent and is estimated to be about 10% of the distance measurement of the analysis (Gelhar and Axness, 1981). A diffusion coefficient of Pb^{2+} in water of 2×10^{-7} cm^2/sec was used in this analysis (Russel, 1961). The results are shown in Fig. 43 where the relative concentration (C/Co) is shown as a function of distance of migration after 35 years. Case A represents the first situation where the adsorption of lead using a $Pb(NO_3)_2$ salt was assumed to be described by a linear isotherm. Case B corresponds to the second calculation where a weighted-mean retardation

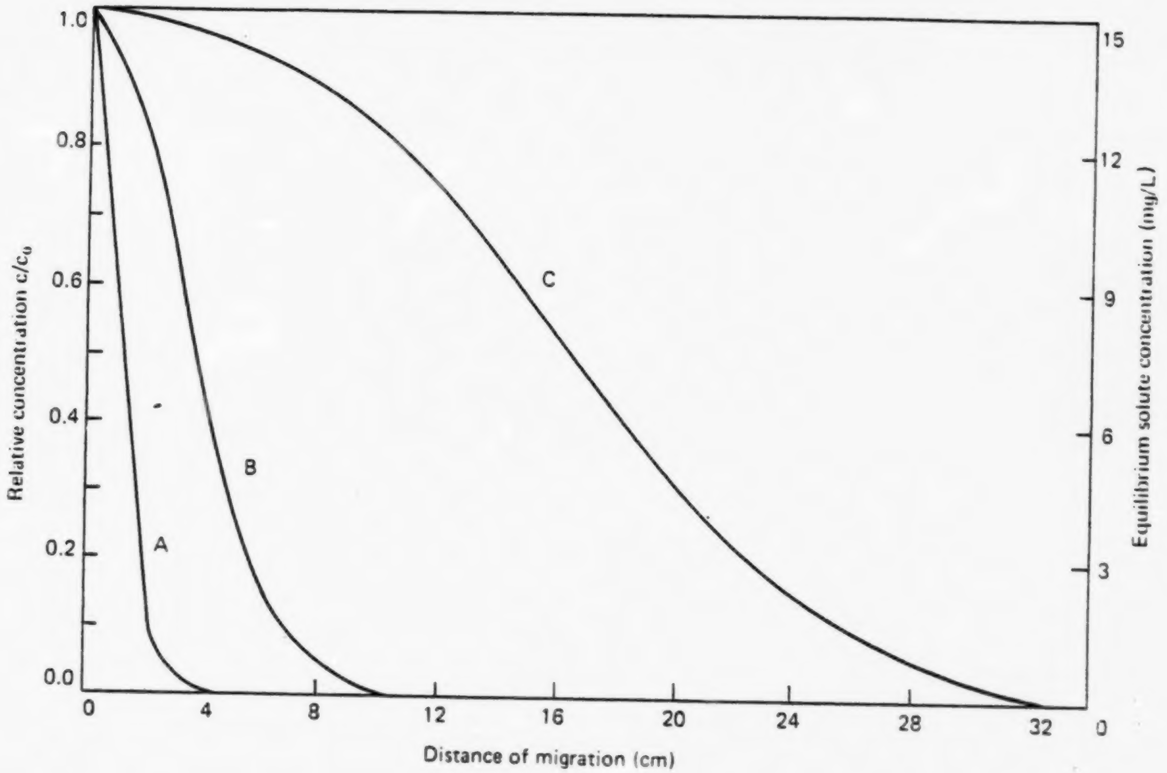

Figure 43. Predicted distance of lead migration in Cecil clay loam after 35 years based on three approaches, case A (linear isotherm assumption, $Pb(NO_3)_2$ salt), case B (weighted-mean retardation factor, $Pb(NO_3)_2$ salt), case C (weighted-mean retardation factor, multicomponent waste extract).

factor was used with the $Pb(NO_3)_2$ solute-soil system. Case C is based on the adsorption of lead from the multicomponent waste extract coupled with the corresponding weighted-mean retardation factor. In this example, taking into account dispersion indicates that the lead may move further than that predicted by an elementary piston-flow model (eq. [40]). The effects of diffusion on the predicted migration distances were negligible (not shown).

There is an element of interpretation when evaluating graphs such as Fig. 43 with respect to making liner estimations. A judgment that must be made is to decide which C/Co ratio, for all practical considerations, translates into the minimum significant concentration. In this hypothetical example, the regulatory agency decided that a lead concentration of less than 0.05 mg/L (the U.S. drinking water standard for lead) would be an operational definition of the compliance concentration.

Assuming that the initial lead concentration is 15 mg/L, the lead concentration of < 0.05 mg/L is predicted to occur at a depth of 5 cm in case A, and at 10 cm in case B. The results for case C represent the fourth level of refinement in this analysis yielding the most accurate liner thickness estimation. After 35 years, the concentration of lead in solution would be reduced to < 0.05 mg/L at a depth of 35 cm, based on these calculations. Consequently, the minimum liner thicknes would be 35 cm. The actual thickness necessary in a field application must be somewhat greater to allow for nonequilibrium conditions, and the normal engineering safety factors. The application of batch adsorption data provides an estimation of boundary conditions, i.e. the minimum thickness.

- In summary, the minimum liner thickness for a hypothetical liner varied from 1 cm to 35 cm, depending on the approach (Table 15). Liner thickness estimations can be refined further if the adsorption data can also be integrated with other information about the design and performance of a site to more accurately predict retention and release of pollutants from an earthen liner. This information would include seepage rate through the cover, fraction of seepage that will pass through the liner, and other water flux information that would allow calculation of the distribution of a pollutant in soil as a function of time and space.

Table 15. Summary of approaches to estimate minimum liner thicknesses.

Flow model	Isotherm Treatment	Solute System	Minimum Liner Thickness (cm)
Piston-Flow[1]	linear	single-solute	1
Piston-flow	nonlinear	single-solute	4
Advection-[2] dispersion	linear	single-solute	5
Advection-dispersion	nonlinear	single-solute	10
Piston-flow	nonlinear	mixture[3]	15
Advection-dispersion	nonlinear	mixture	35

[1] Represented by eq. [40].

[2] Represented by eq. [43].

[3] Laboratory extract.

SECTION 17: LABORATORY PROCEDURES FOR GENERATION OF ADSORPTION DATA

This section of the TRD contains the procedures for the determination of the soil:solution ratio, equilibration time, and other parameters necessary for the construction of adsorption isotherms. The rationale behind these procedures is discussed in the previous sections of this report and should be studied before attempting these procedures. Throughout this section, references are made to other portions of the TRD which elucidate, through discussion and/or example, topics which are relevant to the specific procedural step. It is recommended that those sections be reviewed for further clarification. The following flow diagram (Fig. 44) summarizes the procedures and their inter-relationships.

17.1. SCOPE OF APPLICATION

17.1.1 The extent of adsorption of a chemical (solute) from solution by an adsorbent (i.e., sediment, soil, clay) at equilibrium is measured using these procedures.

17.1.2 These methods are applicable for the generation of adsorption isotherms or curves for inorganic and organic (volatile and nonvolatile) compounds to indicate how the extent of adsorption varies with the equilibrium concentration of the solute.

17.1.3 Contingencies within these methods allow for the construction of adsorption isotherms at various solute concentration ranges.

17.1.4 These methods can be used for constructing adsorption isotherms to study the adsorption behavior of solutes in synthetic waste solutions, laboratory extracts, or field leachates including both aerobic and anaerobic systems.

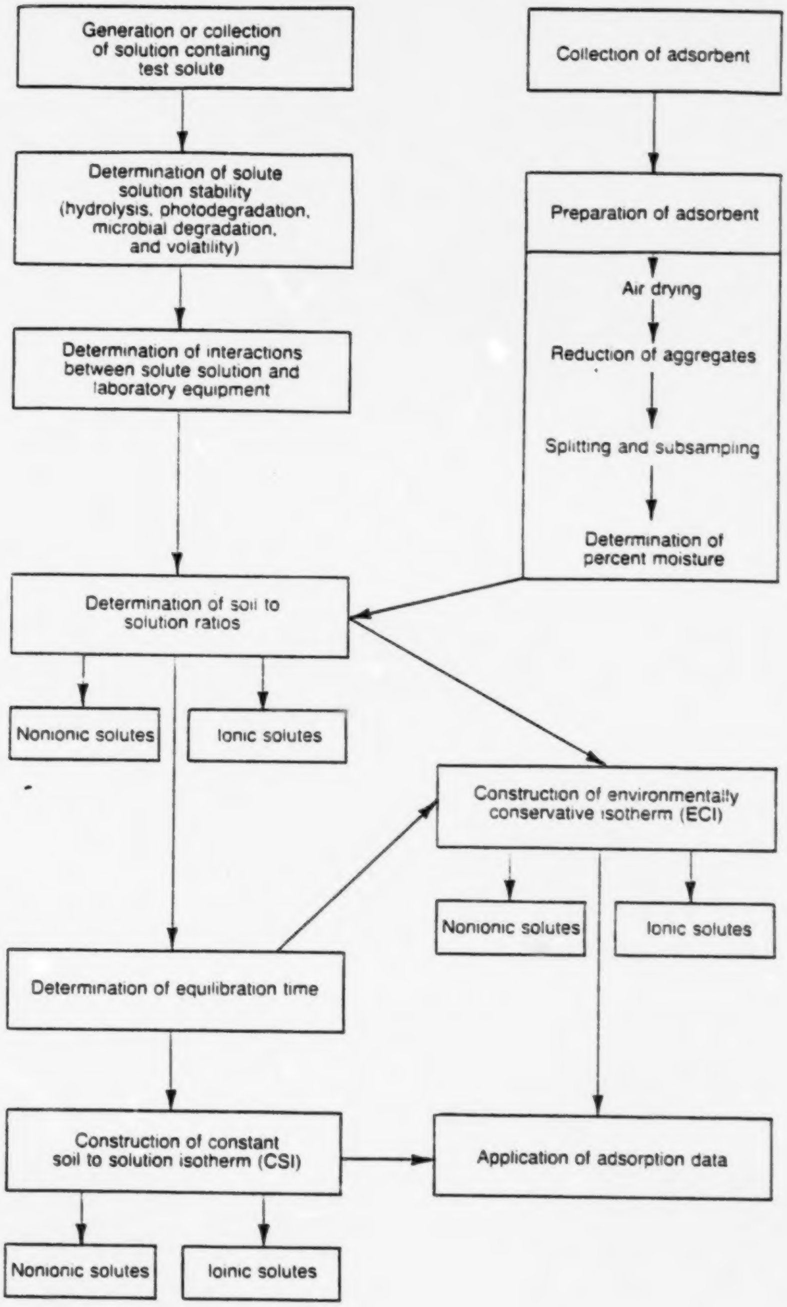
Generation or collection of solution containing test solute
Collection of adsorbent
Determination of solute solution stability (hydrolysis, photodegradation, microbial degradation, and volatility)
Preparation of adsorbent
Air drying
Reduction of aggregates
Splitting and subsampling
Determination of percent moisture
Determination of interactions between solute solution and laboratory equipment
Determination of soil to solution ratios
Nonionic solutes
Ionic solutes
Construction of environmentally conservative isotherm (ECI)
Nonionic solutes
Ionic solutes
Determination of equilibration time
Construction of constant soil to solution isotherm (CSI)
Application of adsorption data
Nonionic solutes
Ioinic solutes

Figure 44. Flow diagram for the procedures for the generation of batch adsorption data.

17.2. SUMMARY OF METHODS

The experimental design of these methods is based on a batch technique as opposed to a column approach. Two general techniques for obtaining adsorption data are incorporated in these methods. The first technique involves mixing a batch of solutions, each with the same volume but containing progressively decreasing initial solute concentrations with a fixed mass of adsorbent in each reaction vessel. The second technique is to mix a batch of solutions, each with the same volume and initial concentration of the solute with different amounts of the adsorbent. In either case, the change in solute concentrations after contact with the adsorbent provides the basis for the construction of adsorption isotherms (see Section 12). The appropriate soil:solution ratios and equilibration times are determined to maximize the accuracy of the adsorption isotherm and to compliment analytical capabilities.

17.3. INTERFERENCES

17.3.1 When dealing with solutes of unknown stability, care must be taken to determine if hydrolysis, photodegradation, microbial degradation, oxidation-reduction (i.e., Cr^{3+} to Cr^{6+}) or other physicochemical processes are operating at a significant rate within the time frame of the procedure. The stability and hence loss from solution may affect the outcome of this procedure if the aforementioned reactions are significant (see Section 4). The compatibility of the method and the solute of interest may be assessed by determining the differences between the initial solute concentration and the final blank concentration of the solute. If this difference is greater than 3%, then the adsorption data generated must be carefully evaluated (see 17.8.5.11).

17.4. TERMINOLOGY-DEFINITIONS

17.4.1 Solute - chemical species (e.g., ion, molecule, etc.) in solution

17.4.2 Solute solutions shall be considered:

17.4.2.1 A solution of reagent water containing a known amount of a solute derived from laboratory reagents.

17.4.2.2 A solution containing a variety of solutes extracted from a material in a laboratory setting using methods such as the ASTM-A or ASTM-B extraction procedures.[1]

17.4.2.3 A solution containing a variety of solutes collected in a field situation representing a leachate or waste effluent.

17.4.3 Adsorption - a physicochemical process whereby solutes are retained by an adsorbent and are concentrated at solid-liquid interfaces (see Section 1).

17.4.4 Adsorbate - chemical species adsorbed by an adsorbent

17.4.5 Adsorbent - substance that adsorbs the solute from solution.

17.5. LABORATORY EQUIPMENT

17.5.1.1 Agitation Equipment - the National Bureau of Standards extractor (rotating tumbler) or equivalent will be exclusively used as the agitation apparatus (see Section 8).

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[1] Neither the EPA Extraction Procedure (EP) or the proposed Toxicity Characteristic Leaching Procedure (TCLP) are recommended. These procedures were designed for waste classification, and were not intended to produce solutions that mimic in situ leachates.

17.5.1.2 Rotation Rate - When performing the procedures involving inorganic, volatile, and nonvolatile organic compounds the rotatary extractor will be operated at 29 ± 2 rpm.

17.5.1.3 Glove box or glove bags - When handling anaerobic adsorbent-solute systems, it may be necessary to conduct these procedures in air-tight enclosures filled with an oxygen free inert gas (e.g. N_2, Ar) to prevent or retard oxidation.

17.5.2 PHASE SEPARATION EQUIPMENT

17.5.2.1 Inorganic Compounds - A filtration apparatus made of materials compatible with the solutions being filtered and equipped with a 0.45-micron pore size membrane filter or a constant temperature centrifuge capable of separating >0.1 micron particles will be used for separation of the solid phase from the solid-liquid suspensions.

17.5.2.2 If filtration is used, the affinity of the filtration membrane for the solute must be evaluted. Failure to do so may lead to erroneous results.

17.5.2.3 Organic Compounds - A constant temperature centrifuge compatible with the reaction containers and capable of separating >0.1 micron particles should be used for separation of the suspension of phases when the solute of interest is organic. The transfer of the organic solute solutions from the reaction containers to centrifuge containers is not an acceptable procedure due to adsorption, volatilization, and other losses; the reaction container should be used as the centrifugation container. Filtration of organic solutions is not a recommended practice (see Section 7).

17.5.2.4 Calculation of centrifugation time may be facilitated by using eq. [1], viz.,

$$t = \frac{9\eta \ln(R_b/R_t)}{2\omega^2 r^2(\rho_p-\rho)} \qquad [1]$$

where $\omega^2 = \frac{4\pi^2 \, (\text{rpm})^2}{60}$

t = time (in minutes)

η = viscosity of water (8.95×10^{-3}g/sec-cm at 25°C)

r = particle radius (in cm)

ρ_p = particle density (g/cm³)

ρ = density of solution (g/cm³)

rpm = revolutions per minute

R_t = distance (in cm) from the center of the centrifuge rotor to the top of solution in centrifuge tube.

R_b = distance (in cm) from the center of the centrifuge rotor to bottom of the centrifuge tube.

To remove particles down to 0.1µm in radius and having a particle density of 2.65 g/cm³ from a solution having a density of 1 g/cm³ may be estimated using eq. [2], viz.,

$$t\ (\text{min}) = \frac{3.71 \times 10^8}{(\text{rpm})^2} \ln(R_b/R_t) \qquad [2]$$

17.5.3 REACTION CONTAINERS

17.5.3.1 Inorganic Solutes - Containers compatible with the rotary extractor should be used in conjunction with inorganic solutes. The containers shall be composed of materials that adsorb negligible amounts of the solute. The containers must have a water-tight closure made of chemically inert materials (i.e., polypropylene, teflon, etc.). The size of the container should provide that the volume of the solid and liquid will occupy about 80% to 90% of the container.

17.5.3.2 Nonvolatile Organic Solutes - Amber glass serum bottles and stainless steel centrifuge tubes or bottles compatible with the rotary extractor and centrifuge are suggested to be used in conjunction with nonvolatile organic solutes. The container must have a water-tight closure made of chemically inert materials (i.e., teflon, plastic, etc.). The size of the container must be compatible with the centrifuge and provide that the volume of the solid and liquid should occupy about 80% to 90% of the container.

17.5.3.3 Volatile Organic Solutes - Amber glass, 125-mL serum bottles (Wheaton No. 223787 or equivalent) fitted with teflon septa (Pierce No. 12813 Tuf-Bond Discs or equivalent) will be used in conjunction with volatile organic solutes. The size of the serum bottle (125 mL) was found to be compatible with several types and brands of centrifuges. This size provides sufficient volume such that the volume of the solid and liquid should occupy 100% of the container (i.e., there should be no head space).

17.5.3.4 As an advisory guide for hydrophobic solutes, commonly available materials for containers can be ranked starting with the material that is most inert with respect to adsorption (T. C. Voice, written communication).

Corex
Pyrex (not appreciably different from Corex)
Silanized serum bottles
Other types of glass
Stainless steel (unacceptable, >95% adsoprtion of PCBs)
Teflon (unacceptable, >95% adsorption of PCBs)
Plastic (unacceptable, >95% adsorption of PCBs)

17.5.4 REAGENTS

17.5.4.1 Reagent grade chemicals will be used in all experiments. Unless otherwide indicated, it is intended that all reagents shall conform to the specifications of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of the determination.

17.5.4.2 Unless otherwise indicated, references to water shall be understood to mean type IV reagent water, as defined in the Handbook for analytical quality control in water and wastewater laboratories, EPA-600/4-79-019.

17.5.5 SOLUTE SOLUTION, ADSORBENT AND TIME (PROCEDURAL) REQUIREMENTS

17.5.5.1 To construct adsorption isotherms for inorganic solutes using these procedures, a minimum of 5 liters of solute solution would be required based on the use of 200-mL samples of the solute solution with 250-mL reaction containers. Investigators using different sized reaction containers should adjust the estimated total volume of solution proportionately.

17.5.5.2 To construct adsorption isotherms using these procedures for organic solutes, approximately 9 liters of solute solution would be required based on the use of 100-mL samples of the solute solution with 125-mL reaction containers. Investigators using different sized reaction containers should adjust the estimated total volume of solution proportionately.

17.5.5.3 The mass of adsorbent required for completion of this procedure will vary depending on the volume of reaction containers, soil: solution ratios, etc. Based on 250-mL reaction containers and the minimum soil:solution ratio of 1:4 (50 g adsorbent per 200 mL of solute solution), about 2 Kg of adsorbent would be required.

17.5.5.4 Approximately 5 to 9 days, excluding analytical time, will be required to complete this procedure.

17.6 EXPERIMENTAL CONSIDERATIONS RELEVANT TO VOLATILE ORGANIC SOLUTES

17.6.1 Stock solutions shall be prepared from pure standard materials (either in the liquid or gaseous phases) or purchased as certified solutions. It is recommended that stock solutions be prepared in methanol. The use of pipetts to transfer solutions is not recommended but rather glass syringes should be used to prevent losses due to volatilization. Because of the toxicity of some volatile organic compounds, preparation and transfer of solutions should be done in a fume hood, and a NIOSH/MESA approved toxic gas respirator be used by the analyst.

17.6.2 PREPARATION OF STOCK VOLATILE SOLUTE SOLUTIONS

17.6.2.1 Place approximately 9 mL of methanol into a 10-mL ground glass stoppered volumetric flask. Allow the flask to stand unstoppered until all methanol wetted surfaces have dried. Weigh the flask with the remaining methanol to the nearest 0.01 mg, and immediately add the test solute, using a syringe, until the change in weight of the flask corresponds to the desired concentration of the test solute in the methanol. Be sure that the drops of solute fall directly into the methanol without contacting the neck or sides of the flask. Dilute to volume with methanol, stopper and mix by inverting the flask several times.

17.6.2.2 Transfer the stock solution into a teflon-sealed screw-cap vial. Store, with none or minimal headspace, at approximately 4°C. All stock solutions must be replaced after 1 month, or sooner if comparison with check standards indicate a loss of accuracy.

17.6.2.3 Stabilize the temperature of the stock solution at 20°C before preparing secondary solutions.

17.6.2.4 Storage of all solutions must be done such that headspace within the storage container is zero or minimized.

17.6.3 PREPARATION OF SOLUTIONS FOR VOLATILE ORGANIC COMPOUND ADSORPTION EXPERIMENTS

17.6.3.1 Place 990 mL of type IV water which has been boiled and cooled to 20°C into each of a series of 1 L clean amber glass bottles. (Generally eight solute concentrations are required for completion of the adsorption procedures.) Seal the bottles with open-top screw caps fitted with teflon lined septa.

17.6.3.2 Inject known volumes of the stock solution prepared in subsection 17.6.2 into each of the bottles. Mix by inverting the bottles several times but avoid excessive shaking which may result in partial loss of the solute.

17.6.3.3 Solutions stored in containers with headspace are not stable and should be discarded 1 hour after preparation if not used in an experiment.

17.6.4 FILLING OF REACTION CONTAINERS

17.6.4.1 Upon immediate completion of subsection 17.6.3 pour each solute solution carefully to minimize agitation into pre-weighed reaction containers or those of known volume (see 17.6.5) and containing known amounts of adsorbent. Fill the containers such that no headspace is present. Gentle shaking of the container to remove trapped air from the adsorbent may be required. Place the teflon-faced septum and aluminum seal on the container and invert to assure no headspace is present. The volume of solution added to the container is assumed to be that volume determined in subsection 17.6.5.

17.6.5 DETERMINATION OF REACTION CONTAINER VOLUME

17.6.5.1 When transferring the solutions prepared in subsection 17.6.3 into the reaction containers, the solutions should be poured quickly but gently into containers of predetermined weight or volume.

17.6.5.2 Because the volume of solute solution is not measured during transfer into the reaction containers, this volume is determined indirectly.

17.6.5.3 The reaction containers to be used in 17.6.4 and each containing the same mass or masses of adsorbent used in 17.6.4 are used to determine the respective container volume for each soil:solution ratio used. Type IV water is pipetted into each container until there is no headspace. The volumes of water added to each of the containers is measured using a calibrated syringe and the container volume is assumed to be that of the volume of waters added.

17.6.5.4 Alternatively, the volume of solution added may be determined by weighing the container containing the adsorbent before and after addition of the solution. The weight is converted to a volume from knowledge of the density of the added solution.

17.6.6 Throughout all experiments the use of blanks is recommended to determine effects of adsorption/desorption from containers as well as losses due to volatilization. Refer to 17.8.5.11 for further dicussion of the use of blanks.

17.6.7 For further information regarding the preparation of solutions for volatile constituents or the analyses of these constituents refer to U.S. EPA test methods 601 and 602 in Methods for Organic Analysis of Municipal and Industrial Wastewater, EPA-600/4-82-057.

17.7. PREPARATION OF MATERIALS TO BE USED AS ADSORBENTS

17.7.1 Samples of adsorbents such as soils, clays or sediments are spread out on a flat surface in a layer, no more than 2 to 3 cm deep. These samples will be allowed to air dry, out of direct sunlight, until they are in equilibrium with the moisture content of the room atmosphere. The sample should be dried enough to facilitate processing and subsampling. Do not oven dry samples (see Section 2). Anaerobic samples should be processed in a similar manner for these and subsequent steps, but these operations should be conducted in a glove box or glove bag filled with an oxygen free inert gas (i.e. N_2 or Ar) to prevent oxidation.

17.7.2 Weigh the entire sample after it has been air dried. Pass the sample through a 2-mm screen sieve. Large aggregates shall be crushed without grinding the sample using a clean mortar and a rubber-tipped pestle. Those aggregates, such as pebbles and stones, that cannot be crushed shall be removed, composited, and weighed.

17.7.3 Mix the sieved material until the sample is homogeneous. Use a riffle splitter, or some other unbiased splitting procedure (ASTM, Method C702-Reducing Field Samples of Aggregate to Testing Size[2], ASTM, Method D2013-72-Preparing Coal Samples for Analysis[3]) to obtain subsamples of appropriate size.

17.7.4 The determination of the moisture content of the air-dried sample shall be done using the ASTM-D2216, Laboratory Determination of Moisture Content of Soils Method.[4]

17.7.5 Determine the mass of the sample required for study corrected for moisture content.

17.6.5.1 Determination of air dry soil (adsorbent) mass equivalent to the desired mass of oven-dried soil

$A = Ms [1 + (M/100)]$

where A = air dry soil mass (g)

Ms = mass of oven-dried soil desired (g)

M = percent moisture

17.8 DETERMINATION OF SOIL:SOLUTION RATIOS FOR IONIC SOLUTES

17.8.1 A series of soil:solution ratios ranging from 1:4 to 1:500 shall be tested and evaluated for the construction of adsorption isotherms (see Sections 9 and 11).

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[2] Annual Book of ASTM Standards, Part 14.
[3] Ibid., Part 26
[4] Ibid., Part 19

17.8.2 The soil:solution ratio is defined as the mass of adsorbent in grams based on an oven-dry equivalent (subsection 17.7.5) per volume in milliliters of solution.

17.8.3 It is recommended that the following soil:solution ratios be used: 1:4, 1:10, 1:20, 1:40, 1:60, 1:100, 1:200, 1:500. The need for soil:solution ratios greater than 1:500 is relatively uncommon for most ionic solutes. In certain circumstances, however, soil:solution ratios greater than 1:500 may be required to meet the criteria outlined in subsection 17.8.5.14; in such cases, 1:1000, 1:2000, 1:5000 and 1:10,000 ratios are suggested. The determination of a soil:solution ratio may be an iterative process, whereby the eight ratios between 1:4 and 1:500 are tested before attempting the extremely "dilute" systems (i.e., 1:1000, and higher). Using an iterative process will reduce the amount of solute solution used, and will help insure that enough solution will exist to complete the entire procedure. Ratios less than 1:4 should not be used due to limitations in mixing.

17.8.4 An example of how different soil:solution ratios are made is given below for an air-dry moisture content of 3%:

Soil:solution ratio (g/mL)	Air-dry weight (grams)	Oven-dry equivalent of adsorbent (grams)	Volume of solution containing solute (mL)
1:4	51.5	50.0	200
1:10	20.6	20.0	200
1:20	10.3	10.0	200
1:40	5.15	5.00	200
1:60	3.43	3.33	200
1:100	2.06	2.00	200
1:200	1.03	1.00	200
1:500	0.412	0.400	200

17.8.5 SOIL:SOLUTION PROCEDURE

17.8.5.1 Calculate the masses of adsorbent samples for the various soil:solution ratios based on an oven-dry equivalent weight (subsection 17.7.5) such that the volume of adsorbent plus solution occupies 80% to 90% of the container for nonvolatile solutes, and 100% of the container for volatile solutes.

17.8.5.2 Weigh the samples of adsorbent to be used in the soil:solution series. If handling anaerobic adsorbent-solute systems, steps 17.8.5.2 to 17.8.5.7 should be conducted in a glove box or bag before placing the containers on the rotary extractor.

17.8.5.3 Place the weighed samples into clean, labeled containers.

17.8.5.4 Pipet the solution containing the solutes (stock solution) into each container containing the adsorbent. The volume of solution should be identical in all containers.

17.8.5.5 Pipet the stock solution into a container containing no adsorbent. This sample will be the "blank." For each set of tests a minimum of one blank, and preferably three blanks, should be tested simultaneously and under identical conditions as the samples.

17.8.5.6 Close the bottles, insuring a water-tight seal, and place on rotary tumbler for mixing.

17.8.5.7 Collect and preserve an aliquot of the stock solution to determine the concentration of the solute(s) before contact with reaction containers, adsorbent, phase separation materials, etc. (initial solute concentration). The volume and preservation techniques of the aliquot will vary depending on the solute and analytical method.

17.8.5.8 Continuously agitate samples at 29 ± 2 rpm for 24 ± 0.5 hours, at room temperature (22 ± 3°C).

17.8.5.9 After 24 hours of agitation, open containers. If the suspensions are anaerobic, return the containers to a glove box or bags prior to opening the containers and make all measurements in the inert atmosphere of the glove box or bag. Observe and record the solution temperature, pH, and any changes in the adsorbent or solution.

17.8.5.10 Separate the solid and liquid phases of each sample, using either centrifugation or filtration (subsection 17.5.2). Determine the electrical conductivity of an aliquot of each supernate (see Section 6). Collect and preserve aliquots of each supernate of sufficient volume to determine the solute concentration.

17.8.5.11 After analysis of all the solutions generated by the soil:solution procedure, a comparison of the initial solute concentration(s) and blank samples is necessary to determine if there was adsorption or desorption of the solute onto or from surfaces other than the adsorbent. If the difference between the blank and initial solute concentrations as calculated using 17.8.5.11.1 is greater than 3%, a correction in the adsorption data must be made.

17.8.5.11.1 Determine the percent difference between the initial concentration and the blank solute concentration:

$$\% D = \frac{(C_o - C_B)}{C_o} \times 100$$

where % D = percent difference

C_o = initial solute concentration (i.e., mg/L, μg/L)

C_B = solute concentration (i.e., mg/L, μg/L) in blank solution.

The difference in concentration shall be subtracted from all adsorption data, excluding the stock or initial concentration value. If % D is a negative value, the solute concentration in the blank was greater than the initial solute concentration. This would imply that there is a contamination problem. Laboratory technique and/or cleaning procedures should be examined.

If % D is a positive value, then the blank solute concentration was less than the initial solute concentration. The difference in concentration shall be added to all adsorption data, excluding the initial concentration value.

17.8.5.12 Using the initial solute concentration and the final solute concentration for the various soil:solution ratios tested, the percent of solute adsorbed can be calculated:

$$\% A = \frac{(Co - C)}{Co} \times 100$$

where: % A = percent adsorbed,

Co = initial solute concentration (i.e., mg/L, g/L etc.), and

C = solute concentration after contact with the adsorbent.

17.8.5.13 Select a soil:solution ratio in which between 10 to 30% of the highest solute concentration was adsorbed. This soil:solution ratio will be used to determine the equilibration time (subsection 17.10), and to generate data for the construction of a constant soil:solution isotherm (CSI). Often, several soil:solution ratios will generate solute adsorption between 10 and 30%. The selection of a specific soil to solution ratio is the investigators' prerogative, with the limitation that it should be one of those listed in subsection 17.8.3 (see Sections 9 and 11).

17.9 DETERMINATION OF SOIL:SOLUTION RATIOS FOR NONIONIC SOLUTES

17.9.1 While finding a suitable soil:solution ratio for ionic solutes must be done empirically, a useful soil:solution ratio for nonionic solutes (hydrophobic organics) may be calculated if the organic carbon content of the adsorbent and the water solubility of the solute are known. The equations and their derivations for determining the soil:solution ratios for non-ionic solutes are given in Section 10.

17.9.2 The soil:solution ratios listed in subsection 17.8.3 most closely matching the calculated soil:solution ratio shall be used throughout this procedure. If the calculated ratio is in the middle of two ratios listed in subsection 17.8.3, the lower ratio (greatest mass of absorbent per milliliter of solute) is recommended to obtain the highest precision and accuracy.

17.10 DETERMINATION OF EQUILIBRATION TIME

17.10.1 Use the soil:solution ratio determined in subsection 17.8.5.13 for inorganic solutes, and subsection 17.9 for hydrophobic organic solutes for the equilibration time determination(s).

17.10.2 A minimum of four agitation times is recommended to determine the equilibration time. Recommended times are 1, 24, 48, and 72 hours, and represent the amount of time the solution and adsorbent are in contact.

17.10.3 Weigh the adsorbent on a oven-dry basis (subsection 17.7.5) and place into clean, labeled containers. If handling anaerobic systems, steps 17.10.3 and 17.10.8 should be conducted in a glove box or bag, before placing the containers on the rotary extractor.

17.10.4 Pipet the solute solution into the various containers at the times designated in 17.10.2. Immediately cap the container and place on rotary extractor at 29 ± 2 rpm at room temperature (22 ± 3°C).

17.10.5 Pipet the solute solution into a container containing no adsorbent; this is the blank and should be agitated for 72 hours.

17.10.6 Collect and preserve an aliquot of the stock solute solution.

17.10.7 Remove the containers at the appropriate times from the rotary extractor and record the solution temperature, pH and any changes in the adsorbent or solution. If handling anaerobic suspensions, return the containers to a glove box or glove bag before opening the containers.

17.10.8 Separate the solid and liquid phases using either centrifugation or filtration (subsection 17.5.2). Determine the electrical conductivity of an aliquot of each supernate. Collect and preserve aliquots of each supernate of sufficient volume for the solute concentration determinations.

17.10.9 Determine the rate of change in the solute concentrations at the various times by

$$\%\Delta C = \frac{(C_1 - C_2)}{C_1} \times 100$$

where $\%\Delta C$ = percent change,

C_1 = concentration of the solute at time t, and

C_2 = concentration of the solute after 1, 24, 48, or 72 hours.

17.10.10 The equilibrium time is defined as the minimum amount of time needed to establish a rate of change of the solute concentration equal to or less than 5% per a 24-hour interval (see Section 13).

17.11 CONSTRUCTION OF THE ENVIRONMENTALLY CONSERVATIVE ISOTHERM (ECI) FOR IONIC AND NONIONIC SOLUTES

17.11.1 The construction of an ECI requires that the soil:solution (subsection 17.8 and 17.9) and equilibrium (subsection 17.10) procedures be completed.

17.11.2 If the equilibrium time as determined by 17.10.9 is equal to or less than 24 hours, the data obtained from the soil:solution procedure can be used in construction of an ECI. However, if the equilibrium time is greater than 24 hours, the soil:solution ratio determination procedure must be redone at the equilibrium time determined by 17.10.9. Refer to Section 12 for discussion of the advantages and limitations of the ECI.

17.11.3 Since subsection 17.9 yields a single soil:solution ratio for nonionic solutes, additional ratios should be selected which bracket the calculated ratio. It is recommended that a minimum of eight soil:solution ratios be used, and that these ratios be selected from those listed in subsection 17.8.3. These ratios will be evaluated as outlined in 17.8.5. When volatile solutes are under study, refer to subsection 17.6 for experimental considerations.

17.11.4 A minimum of five data points should be used to construct an ECI. Soil:solution ratios resulting in less than 10% of the solute being adsorbed should not be used in construction of the ECI (refer to Section 12 for justification). It is recommended that as much data as possible generated by the soil:solution ratios prescribed in subsection 17.8 and meeting the above criteria be used in construction of an ECI. If less than five of the soil:solution ratio data generated in subsection 17.8 meet the criteria listed above, variations in the recommended soil:solution ratios can be used in generating additional data.

17.11.5 Using the data generated by the soil:solution procedure, the amount of solute adsorbed per mass of adsorbent can be calculated.

17.11.5.1 Determination of the amount of solute adsorbed per mass of adsorbent:

$$x/m = \frac{C_o - C}{m} (V)$$

where x/m = amount of solute adsorbed per unit mass of adsorbent,

m = mass of adsorbent in grams added to reaction container,

C_o = initial solute concentration before exposure to adsorbent,

C = solute concentration after exposure to adsorbent at equilibrium, and

V = volume of solute solution added to reaction container.

17.11.6 Construction of an ECI requires that: 1) the x/m value for each soil:solution ratio meets the criteria in 17.11.2, and 2) the corresponding equilibrium concentration value (C) of the solute.

17.11.7 CONSTRUCTION OF AN ECI

17.11.7.1 Using linear graph paper, plot the equilibrium concentration (C) on the coordinate (x-axis) and the corresponding x/m value as the dependent variable (y-axis). Refer to Section 12 for an example.

17.11.7.2 Fit an adsorption equation, using either the Freundlich or Langmuir-type equations to the data plotted in 17.11.5.1.

17.11.7.3 The linear expression of the Freundlich equation is:

$$\log (x/m) = \log K_f + {}^1/n \log C$$

where x/m = amount of solute adsorbed per unit mass of adsorbent,

K_f = a constant,

${}^1/n$ = a constant (sometimes written as N), and

C = equilibrium concentration of solute after contact with adsorbent.

A linear regression can be used to fit a curve through the data plotted in 17.11.5.1, where the intercept equals $\log K_f$ and the slope equals ${}^1/n$. An example using the Freundlich equation is given in Section 14.

17.11.7.4 A linear expression of the Langmuir-type equation is:

$$\frac{C}{x/m} = \frac{1}{K_L M} + \frac{C}{M}$$

where x/m = amount of solute adsorbed per unit mass of adsorbent,

K_L = a constant,

M = a constant, and

C = equilibrium concentration of the solute after exposure to adsorbent.

A linear regression can be used to fit a curve through the data plotted in 17.11.7.1, where the intercept equals $1/K_L M$ and the slope equals $1/M$. Examples using Langmuir-type equations are given in Section 14.

17.11.7.5 From the application of the Freundlich or Langmui-type equations, a coefficient of determination (r^2) can be determined that will indicate the statistical accuracy of the regression used to describe the adsorption data. Examples are given in Section 15.

17.11.7.6 The equation resulting in the coefficient of determination value closest to 1.0 is usually used to generate a curve through the data plotted in 17.11.7.1.

17.11.7.7 The data plotted in 17.11.7.1 and the curve of "best fit," 17.11.7.6, represent an ECI.

17.11.7.8 The following information should be reported with the ECI: 1) temperature at which the tests were conducted, 2) pH and EC of all solute solutions, 3) concentrations of stock (C_0) and blank (C_B) solute solutions and the factor, if any, used to correct data, 4) the soil:solution ratios, their corresponding solute solution volume and adsorbent mass, the initial (C_0) and final (C) solute concentration and the percent of solute adsorbed, 5) the %ΔC for each equilibration time, 6) the equation for the line of "best fit" and the corresponding r^2 value, and 7) a complete description of the adsorbent.

17.12 CONSTRUCTION OF THE CONSTANT SOIL:SOLUTION RATIO ISOTHERM (CSI) FOR IONIC SOLUTES.

17.12.1 Unlike the ECI, where the initial concentration of the solute is constant and the mass of adsorbent varies in each container, the CSI requires that the initial solute concentration varies, and that the mass of adsorbent remains constant. Refer to Section 12 for advantages and limitations of both techniques.

17.12.2 The soil:solution ratio (% A between 10 to 30%) and the equilibrium time (%ΔC <5% per a 24-hour interval), determined in subsections 17.8 and 17.10 respectively, are recommended to be used in the construction of a CSI.

17.12.3 Weigh the adsorbent (mass prescribed by the soil:solution ratio) into clean, labeled containers. If handling anaerobic adsorbent-solute systems, steps 17.12.3 to 17.12.5 should be conducted in a glove box or glove bags.

17.12.4 Make a series of approximately eight dilutions of the stock solute solution (albeit a laboratory extract or field leachate sample) such that there is a progressive decrease in solute concentration. The most dilute solution should contain the solute in a sufficient concentration so that the amount of solute remaining in solution is above analytical detection limits after contact with the adsorbent. The volume of each diluted solution necessary for construction of the CSI will depend upon the size of the reaction container used.

17.12.4.1 The dilution of complex solutions may cause changes in pH, redox potentials, etc. with the subsequent precipitation of the solute(s) (see Section 11). Effort should be made to limit such reactions, and where such actions are not possible or are felt inappropriate, the procedures in subsection 17.11 may be used for determination of adsorption isotherms.

17.12.5 Immediately after the dilutions of the stock solute solution, pipet the diluted solutions into containers containing the adsorbent. Each solution should have a corresponding container with the volume of solution in all containers being equal.

17.12.6 Place the containers on the rotary extractor at 29 ± 2 rpm at room temperature (22 ± 3°C). Agitate for the time determined in subsection 17.10. Collect and preserve aliquots of the stock solute solution, and all dilutions using accepted techniques (e.g. standard methods for the examination of water and waste water[5]).

17.12.7 After the agitation period, remove the containers from the rotary extractor and open. If the suspensions are anaerobic, return the containers to a glove box or bag, then open the containers. Observe and record the solution temperature, pH, and any changes in the adsorbent or solution.

17.12.8 Separate the solid and liquid phases using either centrifugation or filtration (subsection 17.5.2). Determine the electrical conductivity of an aliquot of each supernate. Collect and preserve aliquots of each supernate of sufficient volume for the solute concentration determinations.

17.12.9 Determine the solute concentration in the stock solution, the dilute solutions before (C_0 in equation 17.11.5.1) and after (C in equation 17.11.5.1) exposure to the adsorbent. If significant differences in the blank solutions (subsection 17.8.5.11) were ascertained, the adsorption data must be corrected.

17.12.10 Using the data generated where the various solute concentrations were exposed to the same mass of adsorbent, the amount of solute adsorbed per mass of adsorbent (x/m) can be calculated. Refer to equation 17.11.5.1 for calculation of x/m.

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[5] American Public Health Association. 1975 (14th edition) American Public Health Association, Washington, D.C., p. 38-45.

17.12.11 Construction of the CSI requires: 1) a x/m value for each solute concentration, and 2) the corresponding equilibrium concentration value (C) of the solute.

17.12.12 Construction of the CSI shall follow the same procedure and reporting requirements as the ECI. Refer to subsection 17.11.5 for directions on construction of the ECI/CSI.

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APPENDIX A. SUMMARY AND CHEMICAL COMPOSITION OF THE ADSORBENT SOILS AND CLAYS USED IN THIS STUDY

Eleven different soil materials were used as adsorbents during the development of the batch adsorption procedures. A summary of the adsorbents and their sample locations is given in Table A-1, and a summary of relevant physicochemical characteristics is given in Table A-2, which also includes mineralogical descriptions. The chemical composition of the materials including major elements (Table A-3) and trace constituents (Table A-4) has also been characterized.

The eleven clays and soils represented a wide range in physicochemical properties and characteristics. The Catlin soil is a dark prairie soil (Mollisol), containing a relatively high organic matter content in the surface horizon. It is an important soil agriculturally, and the clay-size fraction is dominated by illite. Mollisols dominate the Great Plains states. The two Cecil soils, Tifton, and soil EPA-14 are Ultisols; highly weathered and acidic soils that are dominated by kaolinite, and iron and aluminum hydroxides. Most of the soils in the southeastern part of the United States are Ultisols. The Vandalia Till is an Illinoian-age deposit and is fairly representative of midwestern glacial tills. It is a sandy till, gray in color, calcareous where unweathered, and the dominate clay is illite. At the sampling site (Table A-1), the Sangamon Paleosol was a buried soil that had formed in the Vandalia till, and was overlain by glacial loess. The Sangamon Paleosol, Vandalia (ablation phase), altered (oxidized) Vandalia, and unaltered (unoxidized) Vandalia tills are a common stratigraphic sequence in Illinois. This sequence is also present at the Wilsonville hazardous waste site at Wilsonville, Illinois.

The soil sample designated as EPA-14 was used by Hassett et al. (1980a, 1980b, 1981) and Zierath et al. (1980) in studies concerned with the adsorption of hydrophobic solutes. The Cecil clay sample from South Carolina was used by Roy et al. (1986) in a study concerned with the adsorption of anionic mixtures. The kaolinite and illite clay samples have also been used in previous studies (see Griffin et al., 1976; Griffin and Shimp, 1976, 1978, and Frost and Griffin, 1977).

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Table A-1. Summary of adsorbents.

Adsorbent	Sample Location	Soil Horizon	Classification
Catlin silt loam	Champaign, Illinois	A_1	Typic Argiudoll
Cecil clay	Spartanburg, South Carolina	B_{2t}	Typic Hapludult
Cecil clay loam	Cecil, Georgia	Ap	Typic Hapludult
EPA-14	Ceredo, West Virginia	A	unknown
Illite	Elizabeth, Illinois	-	-
Kaolinite	Pike County, Illinois	-	-
Sangamon paleosol	Macoupin County, Illinois (near Sawyerville)	B_t	unknown
Tifton loamy sand	Tifton, Georgia	Ap	Plinthic Paleudult
Vandalia Till Member ablation	Glasford Formation Macoupin County, Illinois (near Sawyerville)	B_3	-
altered	(near Sawyerville)	C_2	-
unaltered	(near Eagerville)	C_4	-

Table A-2. Summary of selected physicochemical characteristics of clays and soils used in the development of TRD.

adsorbent	pH(1:1)[a]	sand	silt	clay	organic carbon	CEC[b] meq/100g	surface area[c] (m^2/g)	illite	kaolinite	expandables	Other clay-sized minerals
		%						Clay analysis %			
Catlin silt loam	6.1	11	69	21	4.04	18.1	14.8	55-67	5-15	24-30	chlorite
Cecil clay	4.5	31	12	58	0.34	3.7	36.9	<5	68-92	3-32	gibbsite, goethite hematite
Cecil clay loam	4.6	32	17	51	ND[d]	3.8	29.7	5-6	79-92	2-16	goethite, hematite gibbsite
EPA-14	4.5	2	63	34	0.48	18.9	145[e]	13	37	14	-
Illite clay	7.9	0	0	100	1.81	20.5		70	0	0	30% mixed layer
Kaolinite clay	8.1	0	0	100	0.51	15.1	34.2	8	87	5	quartz
Sangamon paleosol	6.1	45	25	30	0.10	16.7	22.9	33-36	7-14	50-60	-
Tifton loamy sand	4.7	85	9	5	ND	1.9	1.7	0	73-96	4-27	goethite
Vandalia Till											
altered	7.4	45	38	17	0.18	6.6	7.3	71-77	3-10	18-19	-
unaltered	7.5	45	40	15	0.34	4.9	5.6	75-82	4-19	6-9	-
ablation phase	6.4	56	21	23	0.10	10.5	10.6	32-58	2-6	32-39	goethite

[a] pH of a 1:1 soil:water suspension

[b] Catlin exchange capacity

[c] Surface area by N_2 adsorption using BET method

[d] no data available

[e] surface area by ethylene glycol (from Hassett et al., 1981)

Table A-3. Summary of major element composition (in oxide form) of clay and soils used in the development of the TRD (percent).

adsorbent	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5
Catlin silt loam	72.5	0.73	10.8	4.0	0.9	0.71	0.84	2.14	0.1
Cecil clay	44.8	1.15	30.0	10.4	<0.1	0.19	0.07	0.54	0.1
Cecil clay loam	66.2	0.94	20.4	6.8	<0.1	0.19	0.04	0.65	<0.1
EPA-14[a]	ND	ND	ND	6.99	0.71	ND	0.21	2.94	ND
Illite clay[b]	48.5	0.67	24.6	4.11	3.27	1.73	0.14	10.23	ND
Kaolinite clay[b]	46.6	2.45	41.9	0.94	0.57	0.30	0.13	1.49	ND
Sangamon paleosol	82.7	0.43	10.2	2.9	0.50	0.65	0.45	1.49	<0.1
Tifton loamy sand	96.4	0.27	1.3	0.5	<0.1	0.03	0.01	0.05	<0.1
Vandalia									
altered	61.3	0.33	6.7	2.1	9.4	4.66	0.52	2.03	<0.1
unaltered	59.1	0.33	6.5	2.4	9.7	4.95	0.49	2.08	<0.1
ablation phase	83.5	0.35	7.9	2.5	0.6	0.54	0.56	1.98	<0.1

[a] (data from Hassett et al., 1981)

[b] (data from Griffin and Shimp, 1978)

Table A-4. Summary of trace element concentrations in the clays and soils used in the development of the TRD (mg/kg).

	Catlin s.l.	Cecil C.	Cecil c.l.	EPA-14[a]	Illite c.[b]	Kaolinite c.[b]	Sangamon	Tifton l.s.	Vandalia Till		
									altered	unaltered	ablation
As	10	40	4	10	-[c]	-	6	1	6	7	5
B	250	30	25	-	44	46	230	170	172	150	250
Ba	721	117	166	450	-	-	500	44	359	347	460
Be	3	1	2	-	-	-	2	<0.5	2	2	2
Br	8	19	3	-	-	-	<1	2	<7	3	<2
Cd	<1	<1	<1	-	19	<3	<1.3	<1.3	<1.3	<1.3	<1.3
Ce	62	123	81	87	-	-	38	50	25	24	29
Cr	73	206	73	-	-	-	52	20	39	41	43
Co	14	6	3	11	-	-	15	1	8	9	8
Cu	20	45	17	-	-	-	11	<4	15	19	12
Cs	4	10	5	8	-	-	3	2	3	3	3
Eu	1	1	1	1	-	-	1	0.4	1	1	1
Ga	10	37	26	23	-	-	12	2	9	7	8
Hf	12	8	18	3	-	-	-	26	-	-	-
La	36	63	47	46	-	-	28	19	19	19	24
Li	29	29	18	-	-	-	27	4	23	25	22
Lu	0.6	0.4	0.6	-	-	-	0.5	0.4	0.3	0.3	0.4
Mn	834	-	93	216	<390	29	970	90	388	<400	352
Ni	<8	70	<8	-	-	-	<9	<9	<9	<9	<9
Pb	20	44	14	-	94	46	19	<10	<14	13	<9
Rb	82	59	74	200	-	-	79	18	68	68	88
Sb	1	1	0.4	6	-	-	0.6	0.3	0.4	0.4	0.3
Sc	9	25	13	16	-	-	8	4	6	6	7
Se	<2	3	<2	2	-	-	<1	<2	<2	<1	<1
Sm	6	8	8	-	-	-	5	3	3	3	4
Sr	90	<5	<5	<80	-	-	55	<5	75	75	62
Ta	1	2	2	1	-	-	-	1	-	-	-
Tb	1	1	1	1	-	-	-	1	-	-	-
Th	8	24	16	15	-	-	5	6	4	4	4
U	5	7	7	-	-	-	<3	1	<3	<2	<2
W	2	5	2	-	-	-	-	<1	-	-	-
Yb	3	3	3	3	-	-	2	2	2	2	2
Zn	88	40	37	-	38	20	71	<2	42	73	44

[a] data from Hassett et al., 1981

[b] data from Griffin and Shimp, 1978

[c] no data available

APPENDIX B. COMPOSITION OF THE METALLIC WASTE EXTRACT USED IN THIS STUDY AND ASSOCIATED ADSORPTION ISOTHERMS

In order to test and refine the basic batch adsorption procedure for ionic solutes, a metallic waste sample was collected on Nov. 1, 1984 from the Sandoval Zinc Co., near Sandoval, Illinois. Grab samples were taken from a dry slurry lagoon that was used to store metallic scrubber sludges (refer to Gibb and Cartwright, 1982 for additional information). Samples were taken from the surface and from a depth of about one meter. The samples were composited, then air-dried. The relatively fine-grained material was then mixed and poured through a 2-mm sieve.

The laboratory work began by making 20 L of an extract of the metal-rich waste using the ASTM-A water shake extraction procedure (ASTM, 1979). The aqueous extract contained about 0.05% Zn (Table B-1) and lesser quantities of Ba, Ca, K, and Pb. The extract was slightly acidic (pH 6.27) and was used as the stock solution for all of the adsorption experiments. The Sangamon Paleosol sample and the Cecil clay were selected for study since these two soils represented widely different physicochemical materials.

The adsorption of barium, lead, and zinc from the extract by the two soils was investigated and the results were incorporated into the TRD. The adsorption isotherms are shown in Figs. B-1 through B-3, and were generated using the procedures described in the text.

REFERENCES

Gibb, J. P. and K. Cartwright. 1982. Retention of zinc, cadmium, copper, and lead by geologic materials: Cooperative Groundwater Report 9, Illinois State Water Survey - State Geological Survey, Champaign, IL 61820, 113 p.

American Society for Testing and Materials. 1979. Proposed methods for leaching of waste materials: Annual Book of ASTM-A Standards, Part 31, Water, Philadelphia, PA, p. 1258-1261.

Table B-1. Chemical constituent concentrations obtained by the ASTM-A (water shake extraction) performed on the Sandoval zinc slurry (concentrations in mg/L)

pH	6.27
EC(dS/m)	0.17
Al	<0.05
As	<0.08
B	<0.08
Ba	2.25
Be	<0.01
Ca	17.7
Cd	0.45
Co	<0.02
Cr	<0.08
Cu	<0.01
Fe	<0.05
K	6.57
Mg	0.89
Mn	0.64
Mo	<0.02
Na	<0.75
Ni	0.12
P	<0.05
Pb	15.0
Sb	<0.05
Se	<0.04
Si	<0.20
Sn	<0.03
V	<0.08
Zn	550

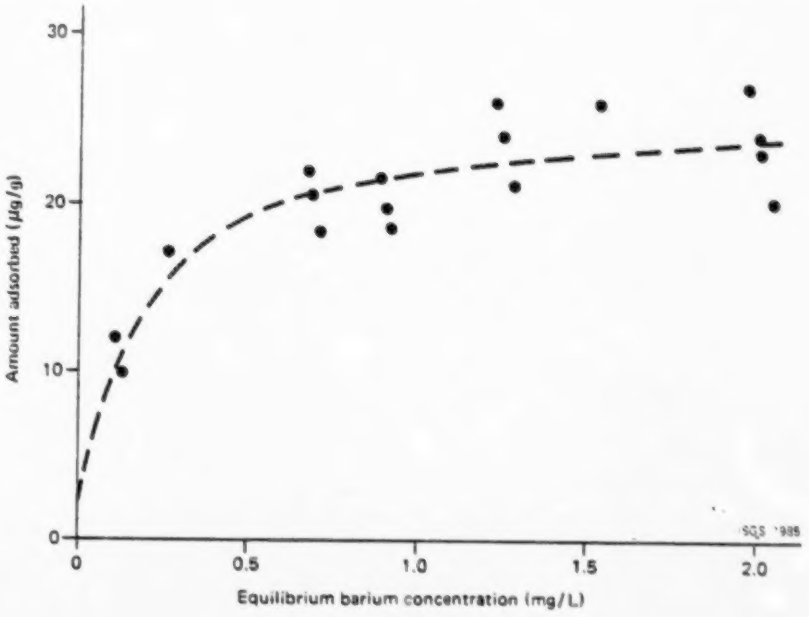

Figure B-1. Barium adsorption isotherm at 21°C with the Sangamon Paleosol from the metallic waste extract. The average pH of the soil-solute suspensions was 5.6.

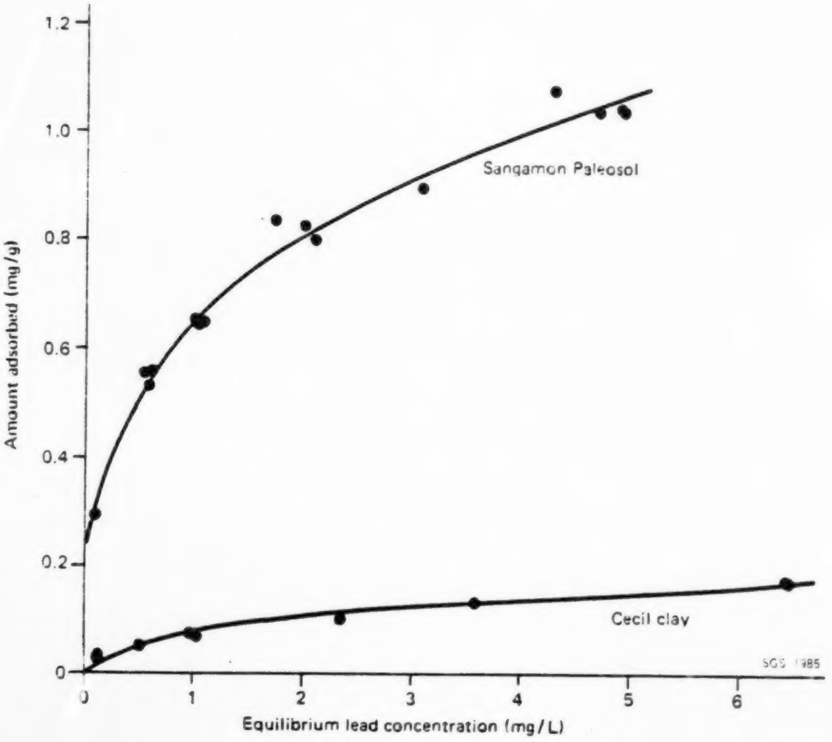

Figure B-2. Lead adsorption isotherms at 24°C of two soils using the metallic waste extract. The average pH of the Sangamon Paleosol suspensions was 5.6, and pH 4.3 for the Cecil clay.

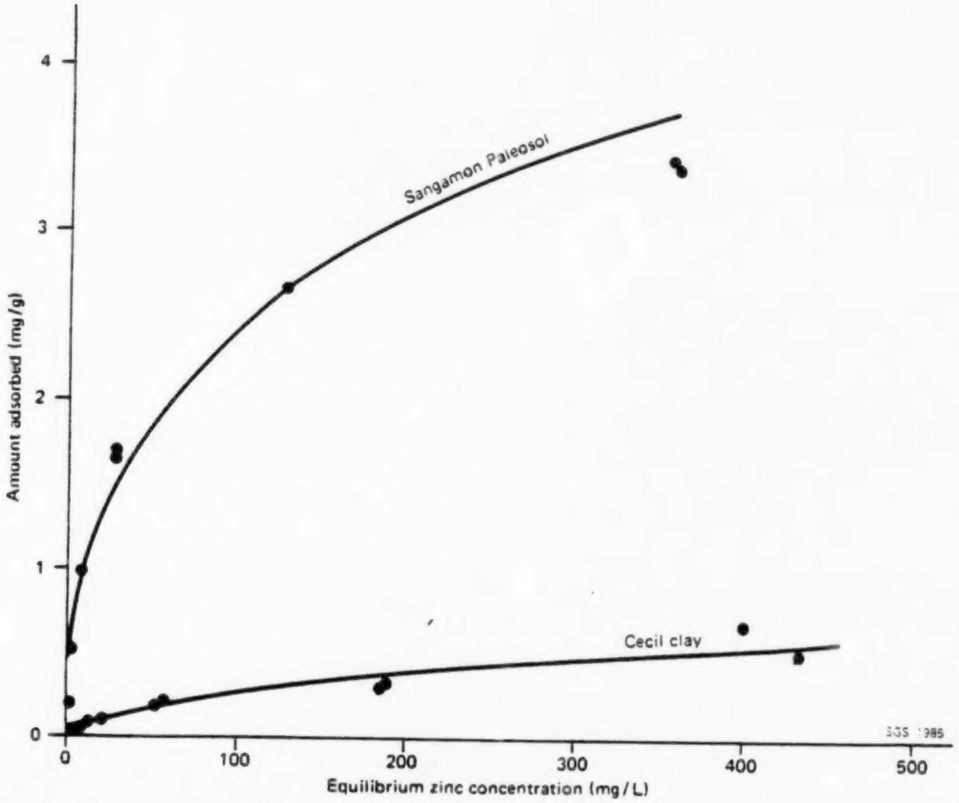

Figure B-3. Zinc adsorption isotherms at 24°C of two soils using the metallic waste extract. The average pH of the Sangamon Paleosol suspensions was 5.9, and pH 4.3 for the Cecil clay.